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# The Journal of the SOCIETY OF DYERS AND COLOURISTS

Volume 67 Number 12

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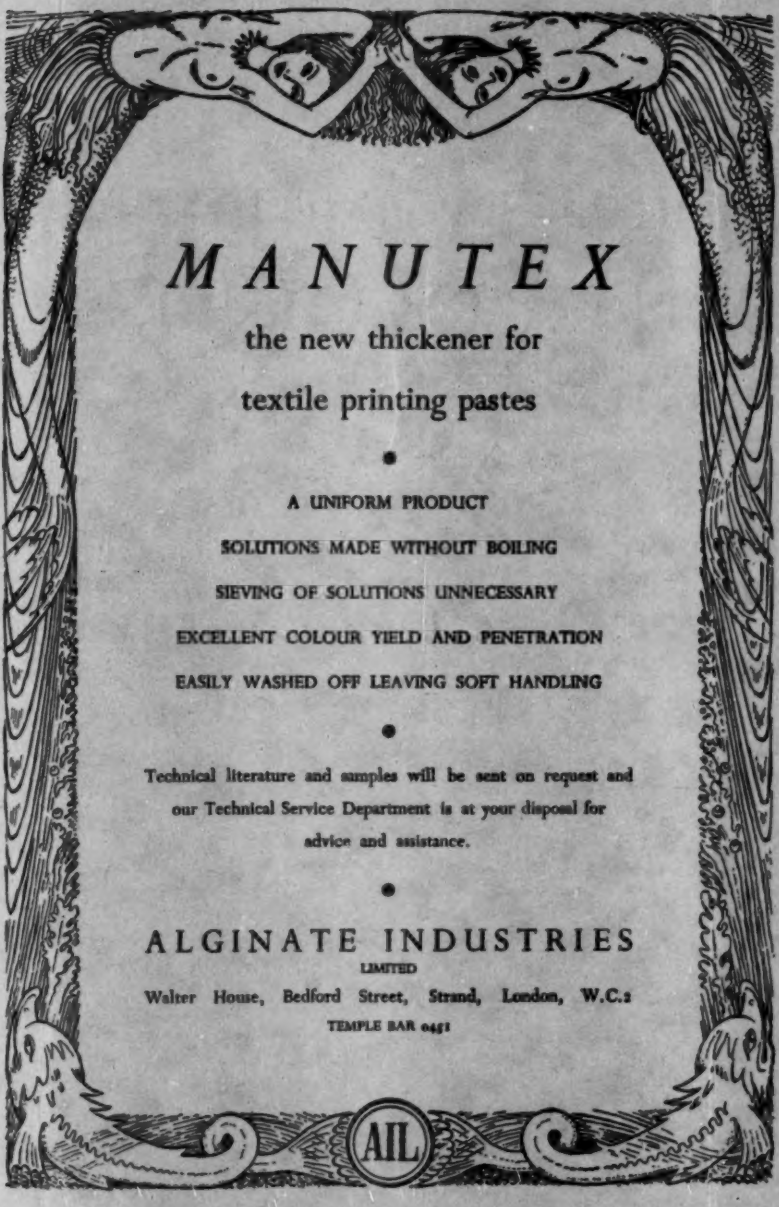

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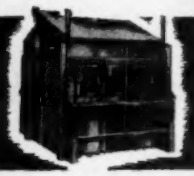

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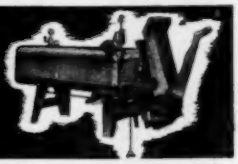

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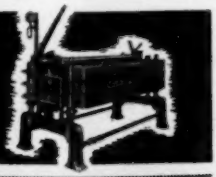

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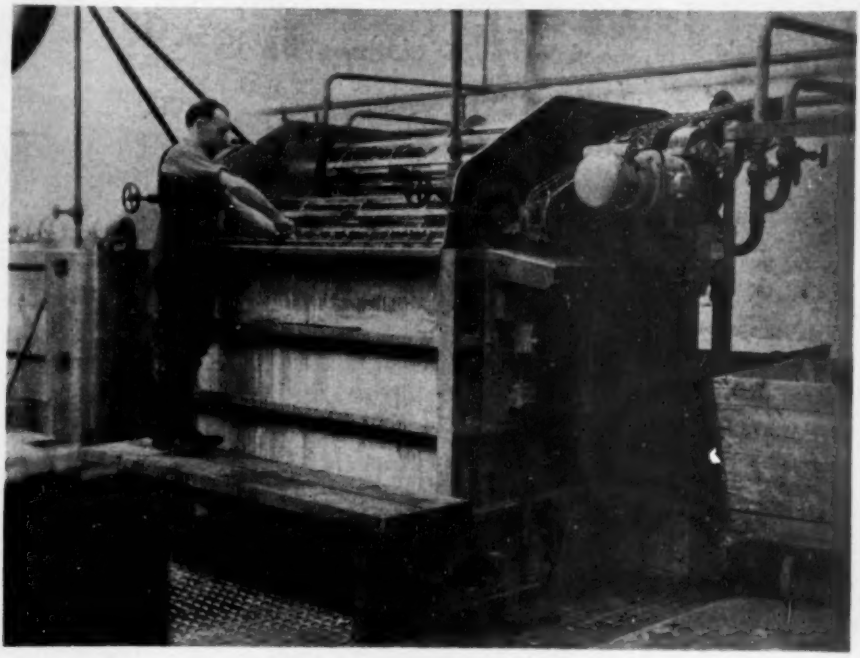

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| | 6 | yellow green |
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**NOTICE TO MEMBERS AND SUBSCRIBERS**

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1951 and pages 253–256 of the July 1951 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, 32–34 Piccadilly, Bradford, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

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# Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Modern Methods for the Investigation of Fibre Structure
*R. L. Elliott and B. Manogue*

The pH Control of Acid and Chrome Dyeing—
II— Single-bath Mordant Dyeing *G. H. Lister*

Radioactive Tracer Techniques and their Applications in Industry
*A. Robson*

COMMUNICATIONS

The Heats and Free Energies of Formation of some Hydrogen Bonds
*M. St. C. Flett*

Diazo Compounds in the Determination of Wool Damage
*M. V. Glynn*

Studies in the Fundamental Processes of Textile Printing.
III— The Transfer of Acid Dyes to Cellulose during Steaming *R. B. Patel and H. A. Turner*

Some Further Investigations into the Fading Rates of Monoazo Dyes
*R. H. Peters and E. Atherton*

The Rôle of Foam in Detergent Action *D. G. Stevenson*

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**ADDRESSES WANTED**

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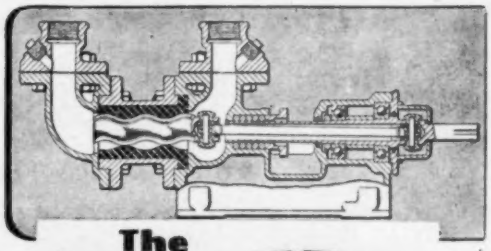
Gunson, H., formerly of 217 Cross Lane, Newsome, Huddersfield
Justice, A., formerly of 35 Cumberland Avenue, Liverpool.
Kulkarni, V. S., formerly of Kirparam Mehtas Street, Gapipura, Surat, India.
Leman, R., formerly of 12 Ballerat Street, Levenshulme, Manchester 19.
Mrozuik, J. S., formerly of 121 Glenfield Road, Leicester.
Presbury, J., formerly of 7 Sparthfield Avenue, Rochdale.
de Franca Pereira F. A., formerly of Rua Presidente Wilson, No. 6-4°-Dt, Lisboa, Portugal.
Rowley, D., formerly of 15 Greenhow Road, Glasgow W4.
Selby, W., formerly of "Westwood", Woodhead Road, Stanningley, near Leeds.
Srinivasan, V. R. (Dr.), formerly of c/o Bangalore Woollen, Cotton and Silk Mills Co. Ltd., Bangalore City, South India.



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# Forthcoming Meetings of the Society

## HUDDERSFIELD SECTION

*All meetings held at Field's Café, Huddersfield at 7.30 p.m., unless otherwise stated.*

1952

Tuesday 15th Jan. — D. Hanson, Esq. *A Chemist in the Woollen Industry*

Tuesday 19th Feb. — F. Jordinson, Esq. *Defective Colour Vision*

Tuesday 18th March — Dr. C. B. Stevens *Some Observations on Dyeing Properties of Modified Wool*

Tuesday 8th April — ANNUAL GENERAL MEETING Dr. G. H. Lister (Sandoz Products Ltd.) *Acid and Chrome Dyes on Wool*

## LONDON SECTION

*All meetings held at 6 p.m. in the Rooms of the Royal Society, Burlington House, Piccadilly, London W.1, unless otherwise stated*

1952

Friday 4th Jan. — J. E. Ford, Esq. and W. J. Roff, Esq. (B.C.I.R.A.). *The Identification of Fibres, New and Old*

Friday 1st Feb. — N. Jackson, Esq. (Courtaulds). *Faults and Damages in Fabrics*

Friday 7th Mar. — Three short papers followed by a questionnaire on *Problems of the Garment Dyer and Cleaner*

It is also intended to hold a Dinner and Dance in the New Year, and to arrange for a lecture to be given in Luton in the spring, on a subject of interest to the hat industry. The date for the Annual General Meeting will be fixed later, for some time shortly after the last meeting of the session.

## MANCHESTER SECTION

1952

Friday 18th Jan. — Details to be announced later, Gas Showrooms, Town Hall Extension, Manchester at 6.30 p.m.

Friday 15th Feb. — E. H. Waters, Esq. and H. Sumner, Esq. *The Effect of Soaping of Vat Dyes.* Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

Thursday 6th March — (Joint with the Textile Institute, Lancashire Section), Dr. A. Landolt (Ciba Ltd.) *Modern Developments in Textile Auxiliaries.* Textile Institute. 7 p.m.

Friday 21st March — Symposium on *Systems of Pack Dyeing.* Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

*Continued on page xxix*

## Manchester Section—*continued*

1952

Friday 18th April — Annual General Meeting, details to be announced later. Gas Showrooms, Town Hall Extension, Manchester. 6.30 p.m.

## MIDLANDS SECTION

*All meetings commence at 7 p.m.*

1952

Friday 18th Jan. — Discussion Meeting with the Leicester Textile Society. *The Dyer's Limitations* (With Particular Reference to Mixed Fibres). College of Technology, Leicester

Friday 22nd Feb. — MIDLANDS SECTION DINNER Black Boy Hotel, Nottingham

Wednesday 27th Feb. — G. G. Taylor, Esq., B.Sc., A.Inst.P. *The Uses of Microscopy in Textile Dyeing and Finishing* (Joint Meeting with the British Association of Chemists). Midland Hotel, Derby

Wednesday 26th March — G. H. Lister, Esq., Ph.D., B.Sc. *The Influence of Dyeing Methods on Fibre Damage.* College of Technology, Leicester

Wednesday 23rd April — G. K. Mecklenburgh, Esq., S. Shaw, Esq., and H. W. Peters, Esq. *Some Developments in Setting and Finishing Nylon Textiles* (Preceded at 6.45 p.m. by the Annual General Meeting of the Section). King's Head Hotel, Loughborough

## NORTHERN IRELAND SECTION

*All meetings to be held in Queen's Hotel, Belfast at 7.30 p.m.*

1952

Wednesday 9th Jan. — Dr. G. H. Lister (Sandoz Products Ltd.) *Wool Dyeing*

Wednesday 13th Feb. — DISCUSSION EVENING

Thursday 6th March — R. C. McKinney, Esq. (Lilliput Laundry and Dyeworks Ltd.) *Commercial Laundering in Practice* (Joint Meeting with Textile Institute)

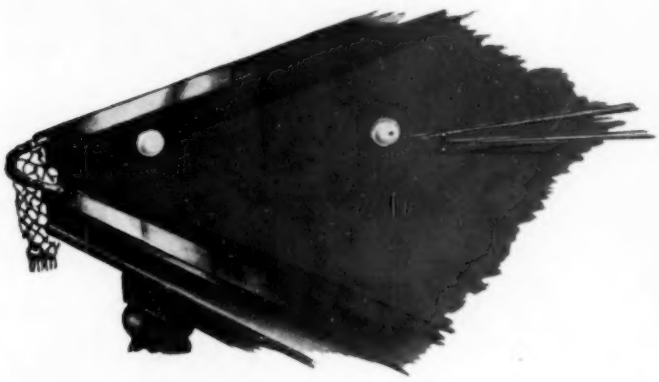
March — ANNUAL GENERAL MEETING and DINNER (date will be announced later)

## SCOTTISH SECTION

*All meetings at 7 p.m., St. Enoch Hotel, Glasgow*

1952

Tuesday 15th Jan. — R. Bury, Esq. *Textile Engraving and Engraving for embossing to the Leather, Glass, Rubber and Paper Trades*



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THE JOURNAL
OF THE
Society of Dyers and Colourists

Volume 67—Number 12 DECEMBER 1951 *Issued Monthly*

# Proceedings of the Society

## CONFERENCE ON "THE TINCTORIAL ARTS TO-DAY"

The Society held a Conference, similar to the four earlier symposia, on "The Tinctorial Arts To-day", at Harrogate, on Thursday–Saturday, 20th–22nd September 1951. The papers were given in the Lounge Hall, the meetings being attended by some 200 members and visitors, including 15 from overseas.

On the Thursday evening, members and visitors were entertained at a Civic Reception and Dance in the Lounge Hall by kind invitation of the Mayor of Harrogate. This was followed, on the Friday evening, by the Society's Dinner and Dance at the Grand Hotel.

### Opening of the Conference

Thursday, 20th September 1951, at 10.0 a.m. in the Lounge Hall

The proceedings began with a welcome to Harrogate from the Mayor (Councillor N. A. FOSTER, J.P.), after which the Conference was formally opened by the President of the Society (Mr. F. SCHOLEFIELD). Mr. Scholefield said that on this occasion the Society had paid special regard to the needs of the practical dyer and colourist. Preprints of the papers (except that of Mr. J. G. Evans) had been circulated some ten days earlier, and would be introduced by the respective authors, except in the case of Mr. J. Baddiley. It was agreed that a telegram should be sent to Mr. Baddiley conveying the sincere wishes of the Conference for a speedy recovery.

#### HISTORICAL RECORDS

A display of material from the Society's collection of historical records was on view in the Lounge Hall throughout the Conference. Among a number of old textbooks were a replica of the first book published in Europe on textile printing, viz. *Traité sur les Toiles Peintes* by M. Q*** (Amsterdam 1760), and a copy of the first British book on the same subject, viz. *A Treatise on Calico Printing* [C. O'Brien] (London 1793). There were also a number of dyer's notebooks and pattern books dating over the last century and a half, the earliest being the *Order Book of Mary Ware, Callico Printer, Crayford, Kent, Sept. 25th, 1773–1775*, and the latest being examples from the Hannay collection, which consists of the laboratory note-books, pattern books, etc. compiled by Mr. J. R. Hannay during his working life in the calico printing industry from 1890 to 1938. Among other outstanding items displayed were a cutting from the first woollen cloth piece-dyed khaki for the British army in 1899, a copy of an *Act for Encouraging the making of Indico in the British Plantations in America* passed by Parliament in 1748, which granted a bounty of 6d. per lb. on indigo imported from the American colonies, notably Carolina and Virginia, the *Memorial of Mr. Cuthbert Gordon Relative to the Discovery and Use of Cudbear and other Dyeing Wares*, being a petition addressed to Parliament in 1785 praying for a reward for his discovery of Cudbear, and a laboratory pattern book dated 1888 from Brooke, Simpson & Spiller's containing original dyeings by Prof. A. G. Green and R. Meldola with notes written by them, the dyeings including Primuline and related dyes.

### The Conference Dinner

The Society's Conference Dinner and Dance was held at the Grand Hotel, Harrogate, on Friday, 21st September 1951, under the presidency of Mr. F. Scholefield.

#### "THE TINCTORIAL ARTS TO-DAY"

After the toast of "His Majesty the King", that of "The Tinctorial Arts To-day" was proposed by—Mr. JAMES EWING, who emphasised that the success of the Conference must be judged not only by the standard of the technical papers and of the ensuing discussions, but also by the stimulation provided for future developments. We were on the threshold of great developments in the dyeing and finishing industry, because of the phenomenal growth of rayon and other synthetic fibres. The development of synthetic dyes had caused the dyer and colourist to require much more than a rudimentary knowledge of chemistry: his need of a thorough scientific training had been rendered imperative by the introduction and development of man-made fibres. Between the two world wars

the textile industry had dealt with five main fibres— cotton, wool, rayon, silk, and linen; now there were in addition six or seven new man-made fibres in commercial use, and many more were likely to follow.

As Dr. Levinstein pointed out in the first George Douglas lecture[1], craftsmanship in the tinctorial arts was already of a high standard some eighty or more years ago in the more limited field open to the users of natural dyes. Since then, the era ushered in by Perkin's epochmaking discovery had seen an ever increasing number of products placed at the service of the dyer and colourist in the pursuit of his vocation, but it had also exacted from him the attainment of more advanced scientific knowledge to enable him to cope adequately with the increasing complexities of his occupation and to appraise the possibilities of the new dyes and chemicals brought forth in abundance. Before and after the first world war the idea (possibly inspired by interested parties) was prevalent that the dyer was being dry-nursed by the great dyemaking companies (particularly the German suppliers) to such an extent that he was in danger of losing his art and descending to the status of a robot. All credence in such a belief should have been dispelled in the early years of the 1914–1918 war when, faced with a famine in dyes caused by the sudden cessation of German supplies, the dyer proved that he had lost little of his skill and initiative by the way he improvised substitutes and collaborated with the British dyemaker in the immense task of replacing the shortages. His resourcefulness played no mean part in enabling our textile industries to survive a gravely critical period. And in the second world war, the British textile industry, aided by the dyer, faced up to much more exacting conditions out of its own resources— another great tribute to the practice of the tinctorial arts.

There was a tendency, both at home and abroad, to belittle the scientific and technical achievements of industry in this country, and we were exhorted to look overseas for ideas as if there were no springs of ingenuity at home. By all means let us look overseas, for it would be foolish to suppose that we could not learn from others. But it was as originators, not as imitators, that we excelled in the past, and it was as such that we should prosper in the future.

That we may have been slow, not in pure science, but in the application of scientific knowledge to large-scale production, must be attributed to the application of our total resources of manpower and materials to the over-riding task of achieving victory in two world wars. Scientific research and technological development to a great extent had had to be shelved. Nor could we overlook the fact that in two generations our young men lost the most receptive years from the standpoint of advanced education and training. We were now feeling the effects of those lost years in the dearth of trained chemists, scientists, technologists, and, most regrettably, teachers, as well as in the present overcrowded condition of our universities and colleges. It was indeed unfortunate that this impediment was being perpetuated under the Military Service Act.

This was not seeking to find excuses for our shortcomings, but rather to eradicate any impression that may have got abroad of British industrialists being complacent and indifferent to progress. Evidence could readily be adduced to correct such an impression— the support given by industry to the great national research associations, the provision of fellowships at universities and colleges, the upkeep of costly research laboratories by many of the larger companies, and the collective efforts of such societies as ours and the Textile Institute. It was encouraging, too, that the Worshipful Company of Dyers was keenly interested in our Industry. All these showed the desire of British industry to keep in the forefront of world progress.

Efforts on an industry level must be supplemented or even led by individual effort on the part of the practical technologist. If he was to make the fullest use of his opportunities, both on his own behalf and on behalf of the industry which he served, he must keep abreast of the latest developments and be *au fait* with contemporary theory affecting his craft. In this connection the meetings of our Society and the reports in its *Journal* made an extremely valuable contribution, the Society being a perfect example of a happy marriage between the academic and the industrial.

It was never wise to dismiss out of hand a new discovery with a prediction that it could not possibly be put to practical use. In it there might be the genesis of some far-reaching development. But a man must have acquired knowledge, experience, and powers of observation if he was to have the prescience to see some application which had escaped the notice of others. At the same time, to keep our feet on the ground, it was well to remember one of Carlyle's dicta—

> Our grand business undoubtedly is not to see what lies dimly at a distance, but to *do* what lies clearly at hand.

In the chain of textile processes, dyeing formed a link the relative importance of which (as Mr. Crossley had pertinently remarked[2]) was by no means represented by its proportion of the price of the finished article. Being the last stage of production, dyeing could either make or mar the finished cloth. Salability of the cloth depended greatly upon the exercise of the dyer's skill. His responsibility would grow in the near future when, as recent reports indicated, competition from Japan and Germany— to mention only two sources— could be expected to increase in severity. All the dyer's skill would be called into play to crown the efforts of the spinner and weaver in the production on a large scale of fabrics of superior and distinctive quality and appearance, because in the production of such fabrics lay our chief hope of sharing in the world's export trade in face of competition from low-wage countries.

Thus the scope for and the importance of the exercise of the tinctorial arts were to-day greater than ever. Mr. Ewing was confident that the high

[1] Levinstein, H., J.S.D.C., **65**, 209, 533 (1949).

[2] Crossley, W. R., J.S.D.C., **66**, 265 (1950).

standards of the past would be emulated in the present and the future in the fulfilment of the art of adding utility, grace, and beauty to the products of our industries.

Dr. C. M. WHITTAKER (*a Past President of the Society*), in responding to the toast, suggested, on the basis of the information supplied by his olfactory organs, that Harrogate might well consider the possibility of relieving the shortage of sulphur from which the dyeing and finishing industry was suffering.

It was most appropriate that Mr. Ewing, as chairman of the large organisation which was rapidly becoming a Commonwealth dyers' association, should have been asked to propose this toast. Colour was the first salesman of every textile to the ultimate consumer. It did not matter how skilfully it was woven or knitted; if it were not appropriately coloured Miss 1951 would turn up her pretty nose and pass by on the other side, like the Pharisees. That view was supported by the great French Minister Colbert, who wrote in 1672—

> All visible objects are distinguished and recommended by colours: but for purpose of commerce it is not only necessary that they should be beautiful but that they should be good and that their duration should equal that of the material they adorn.

Though written in 1672, it was equally true to-day and worthy to be adopted as the slogan of the Society.

We were now entering the battle of the man-made fibres. We dyers were entitled to say to the fibre engineers not "Go to the ant thou sluggard" but "Imitate the silkworm". The silkworm was the only machine which had solved the problem of orientating the micelles to give adequate strength whilst retaining maximum dye absorption. Natural silk had the greatest dye-absorptive power of any fibre, as every poor rayon dyer knew when he was given a heavy shade on natural silk to match on rayon—particularly one of those heavy shades beloved in the natural silk tie trade. One could put a barrel of dye in the dyebath, but the rayon was incapable of absorbing it. The fibre engineer must remember that his fibre was useless unless it could be dyed. One could not dye without swelling.

### "OUR GUESTS AND VISITORS"

Mr. F. SCHOLEFIELD (*President of the Society*), in proposing the toast of "Our Guests and Visitors", welcomed the civic dignitaries of Harrogate, and thanked the Mayor and Corporation for their hospitality and their helpfulness in many ways. Smollett had described the situation of Harrogate as "a wild common, bare and bleak", but the presence of the sulphur, chalybeate, and magnesia springs had led to the present flourishing and beautiful town, to which the Society had returned to hold its conference.

The presence of Mr. Ewing was evidence of the continued interest in the Society shown by the great companies in the industry. The Society was indebted to those who had contributed papers to the Conference, and was especially pleased to welcome visitors from overseas, notably from France, Holland, Switzerland, and the U.S.A. Finally, the Society was delighted that so many ladies had graced the dinner.

Councillor E. ROBINSON (*Deputy Mayor of Harrogate*), in responding to the toast, said that, being accompanied by both the Mayoress and the Deputy Mayoress, he had two strings to his bow. He had taken due note of the suggestion regarding sulphur production in Harrogate. Perusal of the Society's *Journal* had impressed him with the value of the Society's work, but the sight of the complex chemical formulæ was so overwhelming that he felt quite incapable of penetrating more deeply the mysteries contained therein. He felt it a high tribute to Harrogate that the Society had returned so soon to hold its conference there. Finally, he would like to express the gratitude of all the guests for a very enjoyable evening.

THURSDAY MORNING, 20th SEPTEMBER 1951

*Chairman* — Mr. G. S. J. White

# Milestones in the Production of Synthetic Dyes for Cellulosic Fibres

C. M. Whittaker

The introduction of the various classes of dyes for cellulosic fibres is dealt with in historical sequence from Mauvein to the latest phthalocyanine compound. Some of the prominent members of each class are briefly mentioned, giving the year of their introduction. The effect of their introduction on the dyeing industry as seen by the author is briefly outlined.

This paper reflects the personal impressions of the more important dyes as represented by their specific impact on my own specific activities during fifty years in the textile industry. I am certain that many, according to their own specific activities, will consider that there are many omissions.

Mauvein is, naturally, the first milestone in synthetic dyes for cellulosic fibres, bearing the date 1856. What impresses itself on my mind in again reading the literature of W. H. Perkin's life is that the first synthetic dye forced its maker to provide technical service to the commercial user—a service which, with the vast increase in the variety of dyes, has grown to an enormous scale. Now that dye manufacturers have entered the field of synthetic fibres they are finding servicing demands to be ever widening. Robert Pullar with W. H. Perkin worked out the method of dyeing cellulosic fibres with Mauvein.

The next milestone bears the date 1863, when Lightfoot discovered Aniline Black, which was the first example of a synthetic dye actually produced on the fibre by the dyer himself—a discovery which has been used for colossal quantities of cellulosic textiles. Its commercial history in Great Britain parallels the rise and fall of the Roman Empire with the Huns being replaced by the Japanese, whose competition forced the closing of huge plants in Great Britain.

The basic dyes supply the next series of milestones. I have always felt that it was a tragedy that these dyes, of still unsurpassed brilliant hues coupled with extreme fugitiveness, were discovered so early in the development of synthetic dyes. Their lack of fastness retarded the use of the then so-called "Anilines" for years, and provided the old-time dyers with a strong justification for their hostility and conservatism. The other misfortune was that these brilliant hues found their way into the textile designers' studios, and were repeatedly sent to the dyers for reproduction in a fastness for which there were no comparable dyes. For example, Malachite Green was discovered in 1878, but the dyer had to wait until 1920 for Caledon Jade Green, which first enabled him to give with confidence a Jade Green hue suitable for soft furnishings and washing fabrics. Meantime dyers were compelled to write thousands of letters regretting inability to dye the hues requested. The leading basic dyes appeared in the following sequence— Magenta (1858), Methyl Violet (1866), Methylene Blue (1876), Malachite Green (1878), Auramine O (1883), whilst Rhodamine B followed in 1887 and Rhodamine 6G in 1892.

The next milestone bears the date 1868, when synthetic Alizarin gradually replaced Madder, from which were developed many other Alizarin dyes, which were used mainly by the printing industry for cellulosic fabrics. The march of time subsequently compelled Alizarin to yield pride of place to the azoic dyes, of which the first— from Naphtol AS — was marketed in 1912. To Thomas and Robert Holliday belongs the credit of first producing azoic dyes on cellulose. They discovered this in 1880, but themselves exploited it as dyers, so that it did not have the same impact on the dyeing industry as the introduction of Paranitraniline Red in 1889. The Hollidays used $\beta$-naphthylamine→$\beta$-naphthol, whereas Meister Lucius und Brüning advocated *p*-nitroaniline→$\beta$-naphthol. Para Red became a commercial standard and was exploited most successfully by the calico printing industry.

In 1912 a new naphthol— Naphtol AS— was marketed. This had many practical advantages over $\beta$-naphthol, though more expensive. Since 1912 a large series of compounds have been developed which provide a range of shades of a brilliance and fastness hitherto unattainable. For the printing trade the subsequent introduction of the Rapid Fast, Rapidogen, and Rapidazol ranges was a great advantage.

The year 1884 is outstanding for the introduction of the first Direct Cotton dye by Paul Boettiger, marketed as Congo Red, soon to be followed by the superior Benzopurpurine 4B of Duisberg. This discovery blazed a trail, the end of which is not yet in sight, but considerations of space compel a condensed treatment of the step-by-step additions of improved fastness and shade which have been marketed in this class of dyes and which are used in so many branches of the dyeing industry. Dianthine 4B (1888)— the first red fast to acids— Curcumines (1883), Chrysophenine G (1886), Mikado Orange (1888), Erika Pink (1888), Diamine Fast Red F (1889), Black BH (1890), Sky Blue FF (1891), Pluto Black (1896), Columbia Black FF (1898), Direct Deep Black E (1901).

I think everyone must be amazed how some of the earliest and least fast of the direct cotton dyes hold their own in many branches of the dyeing industry. Benzopurpurine 4B is still not a back number. It is a measure of the conservatism of the average dyer coupled with the fact that there still are many lines of merchandise for which fastness to light and washing are not demanded.

The 1887 milestone has Primuline and the name of A. G. Green engraved on it. It marks the initiation of the diazotisation and development of a new dye on cellulose from another dye. Primuline →$\beta$-naphthol gave the first one in Primuline Red. The tragedy of the story of the failure of Brooke, Simpson & Spiller Ltd. to patent it has often been told, and it is an interesting speculation how the firm would have fared had they done so. Read Holliday & Co. very quickly found the secret, and Elbel, a German chemist at Huddersfield, went to

Kalle & Co. A.-G. and showed them how to make it.

Dehydrothio-*p*-toluidine— always produced simultaneously in the Primuline melt— spawned the Fast Yellow B type. Read Holliday were so slow that they sold their dehydrothio-*p*-toluidine to Leopold Cassella & Co.: how the latter must have laughed at getting it without the Primuline. It is interesting to reflect how the different makes of the Fast Yellow B type varied in their behaviour in a sodium sulphide bath. Owing to the poor light fastness of the Sulphur Yellows, Fast Yellow B was frequently used as the yellow component in compound shades of sulphur dyes in dyeing loose cotton for the Colne Valley trade. Diamine Fast Yellow B was superior in this respect to any other make of the same yellow.

Historically it may be of interest to recall that Read Holliday developed a series of direct cotton dyes under the name of Titan. Their affinity for cellulose was so weak compared with the benzidine class that they rightly failed. Titan was an unfortunate choice of name.

The Janus Dyes were marketed in 1896. I was a student at Leeds, and Professor Hummel busied himself with them, but they likewise failed commercially.

Cachou de Laval is engraved on the 1873 milestone as the first sulphur dye made by the fusion of organic matter with sodium sulphide. This reaction was neglected until Vidal produced the first Sulphur Black in 1893 from *p*-aminophenol. My first job at Read Holliday in 1899 was to study the nitration of phenol, for they were making an excellent Sulphur Black of the Vidal type— Cross Dye Black 4B. Vidal Black required chroming to develop it, so when in 1900 the Berlin Aniline Co. marketed Sulphur Black T Xtra made from dinitrophenol, which did not require chroming, the Vidal Black type fell completely out. I know that at that time at Huddersfield we fused every organic product we could lay our hands on to see if it gave a sulphur dye. The range of sulphur dyes was gradually extended to blues— Pyrogene Direct Blue (1900), Immedial Indone (1902), Sulphur Brown (1902), Sulphur Yellow, Sulphur Green, but the bright red is still missing. The Immedial leuco dyes found acceptance in package dyeing.

The latest development is the M brands of the Thionol dyes, which are water-soluble but without affinity until sodium sulphide is added. These suggest intriguing possibilities in the way of aiding penetration of packages and thick cloths. The analogy with the pigment pad process is not exact, but the lack of affinity of the water-soluble sulphur dye does permit of thorough impregnation of a difficultly penetrable package or cloth before the potential affinity of the dye for cellulose is liberated.

The 1897 milestone has synthetic Indigo engraved upon it, from which the Ciba Blues were derived in 1907. Before the halogenated Indigos were marketed, it may be of interest to record, Sansone offered Read Holliday a process for brominated natural Indigo before Ciba Blues were marketed, but his terms were so high that the offer was not investigated in detail.

1901 is a very important milestone, with Indanthren engraved upon it— a discovery which has made many a dyer walk through the Slough of Despond, and a dye with which it has taken almost fifty years to evolve the present piece-dyeing practice for vats.

I should be remiss if I did not recall the milestone 1904 and the work of Bernthsen in producing Hydros, whose indispensability has been emphasised by the present sulphur shortage. 1908 saw the Thioindigo series marketed, whilst it was not until 1920 that Caledon Jade Green enlarged the dyer's range most acceptably.

Hydron Blue— the most overrated vat dye in my opinion— was discovered by Herz in 1908. It was common talk at the time that the Badische Anilin- & Soda-Fabrick endeavoured to suppress it, but after undisclosed manœuvres Cassella marketed it. It was at least known that a chemist was sent to prison. Its production brought carbazole to the front as an intermediate.

Indigosol O appeared in 1925, and was followed later by the range of Indigosols and Soledons. Their adoption was slow at first, but they are firmly established now.

It was obvious to aim at direct cotton dyes equal to vat dyes in fastness to light, and big advances in light fastness have been made coupled with an undesirable tendency to overstate the fastness.

The cyanuryl reaction produced in 1922 the first dyes based on it, viz. Cibanone Red B and 4B, Cibanone Orange R, and Cibanone Yellow 2GR, which were followed by the introduction of the cyanuryl (triazine) ring into the molecule of azo dyes, yielding the direct cotton dyes of improved fastness to light, Chlorantine Fast Green BLL and Chlorantine Fast Red 5GLL.

In my experience the only direct cotton dye which equals vat dyes in fastness to light was first marketed in 1930 as Solophenyl Red Brown. The exceptional and unequalled fastness to light of one dye in a class may be, of course, a temporary handicap, because there are no dyes of its class available for making mixed shades and, therefore, an unbalanced fade will result. Before Sirius Supra Grey VGL was marketed, there was no Direct Black, Blue, or Green of equal fastness to the available fast-to-light yellows and oranges, and so balanced fades were extremely difficult to obtain.

The outstanding discovery of Monastral Blue was not of immediate interest to the dyer, but to the producer of spun-dyed rayons it was most acceptable. Curiously enough, as a pigment its monochromatic character was of the highest value, but when spun into cellulose acetate rayon it yields a dichroic shade. At the time of writing, however, three valuable dyes have been derived from Monastral Blue— Durazol Blue 8GS of good fastness to light though poor affinity in 1937; and Alcian Blue in 1949, which has filled a gap in the calico printer's fast shade range. Recently the Farbenfabriken Bayer have marketed Phthalogen Brilliant Blue F3G, a water-soluble phthalocyanine compound which is colourless but which on subsequent treatment with metal salts at 100°c. gives a bright, fast, insoluble phthalocyanine dye.

## Discussion

Mr. F. Smith: Hydron Blue has not been overrated for the purpose for which it was intended, mainly workmen's overalls. In 1913 as a test of its fastness Messrs Cassella & Co. had a large number of workmen's overalls made, one pant dyed with Hydron Blue, the other with Indigo. As one went through the streets of Mainkur on washing day, when these goods were hanging out on the line, it was very obvious which was the better dye.

Dr. Whittaker: Hydron Blue was also used in the towel trade. I was told by the chairman of a large group of yarn dyers that it received more complaints regarding fastness of Hydron Blue dyeings than of any other dye they used.

Mr. H. Boothroyd: Dr. Whittaker stated in his paper that Hydron Blue was the most overrated *vat* dye. Since it is generally agreed that Hydron Blue is a product which falls between vat and sulphur dyes, Dr. Whittaker's statement can be accepted, since he is comparing Hydron Blue with an average true vat dye, which undoubtedly reveals the superiority of the latter.

Mr. R. L. Hill: Although the new solubilised form of diphenyl-base black, Solanile Black (Fran), which formed the subject of a recent paper by Jomain and Zuber to the Manchester Section, is at present of interest mainly for textile printing, it is being applied to piece goods by padding, and it is hoped to extend its application to the dyeing industry.

Dr. T. A. Forster: What is the author's opinion of those selected direct dyes for the dyeing of cellulose materials which are greatly improved in washing fastness by aftertreatment with copper salts?

Dr. Whittaker: Copper salts have the undesirable effect on viscose rayon of making it less water-absorbent, and therefore it presents difficulties if the yarn has to be sized subsequently; the yarn is also liable to wind less easily owing to being harsh and sticky. My being concerned with rayon dyeing for the most part of my activities has contributed to my omission of these dyes. On my recent trip to Canada I found them being used for the dyeing of cellulosic fibre stock to be subsequently blended with wool.

Mr. S. Burgess: The difficulties of application of the aftercoppering dyes (many are Class C dyes) are being overcome, and they can play an important part in the attainment of light and washing fastness. One great difficulty is price, as the shades will be heavy and some can be very expensive indeed. Dyers and their customers should discuss this matter, so that dyers can take full advantage of the new discoveries of the dyemakers.

Mr. J. Boulton: Many ordinary Class A and B dyes, aftertreated with e.g. Fibrofix and a copper salt, give equal wet fastness to that given by the aftercoppered dyes, are satisfactorily fast to light for many uses, and are not less bright. The comparison on a dye–cost basis of these two dyeing methods is very favourable to the ordinary dye treated with Fibrofix.

# Developments in the Application of Sulphur Dyes to Loose Cotton and Yarns

H. Birchall

The evolution of sulphur dyes is briefly reviewed, and the dyeing of loose cotton and sliver outlined. Yarn dyeing is described under the headings of hank, warp, and package dyeing, and the aftertreatment of sulphur dyeings is discussed. Finally, the application of water-soluble types of sulphur dyes is described.

In considering developments in the application of sulphur dyes, it is worth while paying a little attention to the nature of these dyes, their history, and their properties, in order to relate these to the progress made in their application.

In 1873 the first sulphur dye— Cachou de Laval —was prepared by melting organic substances such as sawdust with sulphur and sodium sulphide at 100–300°c., the shade becoming deeper as the temperature increased.

This dye was fast to washing, alkalis, and acids, and was moderately fast to light; it was welcomed by cotton dyers, but the range was not extended until 1893, when a French chemist, Raymond Vidal, discovered Vidal Black, which was prepared by heating benzene or naphthalene derivatives with an alkali-metal polysulphide melt. The resultant product dyed cotton from a sodium sulphide bath and required oxidation with dichromate.

This was undoubtedly the turning point in the manufacture of sulphur dyes, and from 1896 Read Holliday introduced a range of grey, drab, brown, and black sulphur dyes by the action of sulphur and alkali sulphides on a variety of organic substances; the same firm was responsible for the introduction of blues in 1898, a further step towards a complete range.

Using sulphur monochloride as a sulphurising agent, the Clayton Aniline Co. introduced in 1898 a series of sulphur blacks, and shortly after this there followed Immedial Maroon, bright blues of the Immedial Pure Blue type, and by 1901 yellows, oranges, and greens.

As long ago as 1908, Indocarbon Black (reasonably fast to chlorine) was made by Leopold Cassella & Co., followed by the Hydron Blues, which had improved wet fastness and better fastness to chlorine.

This comparatively rapid progress in the development of the range seemed to reach a certain stage, and was then retarded by the inability to produce true reds and bright shades generally, and also by the indeterminate composition of the dyes due to their method of manufacture, which resulted in commercial types containing an amount of matter insoluble in the normal alkaline sulphide liquors used for dyeing, thus causing sulphur dyes to be regarded as somewhat "dirty" and unfit for some methods of application.

The recent introduction of Thionol Ultra Green BS (ICI), which is a bright and clean colour, suggested that there may be scope for development, but from information available it appears that this dye is produced by synthesis and is not likely to form the basis of a range with similar brightness and properties.

The lack of cleanliness has been overcome to a great extent, and reference to the Immedial Leuco dyes and the water-soluble Thionol M brands will be made in discussing the application of sulphur dyes.

Apart from specialities such as these, sulphur dyes may very broadly be considered to be intermediate in all-round fastness properties between direct cotton dyes on the one hand and vat dyes on the other.

It is, however, unwise to generalise on a range of dyes (even vat dyes), and there are great disparities in the properties of sulphur dyes; e.g. in wet fastness the bright blues, greens, violets, and corinth browns are inferior to the ordinary browns, blues, and blacks. In light fastness the yellows, oranges, and browns are inferior to the blues, greens, and blacks.

This brief survey of the history, scope, and properties of sulphur dyes will be sufficient to provide an introduction to the application of these dyes to loose cotton and cotton yarns in various forms.

The development in application is due to two main causes—

(1) Progress in machinery, making for greater efficiency and productivity

(2) Development in variety and purity of the dyes, enabling them to be used for purposes and by methods previously impracticable.

The various methods of application will be considered first in relation to the general range of sulphur dyes, the leuco and water-soluble types being discussed separately.

Sulphur dyes, intelligently selected, can be used for a wide variety of trades and can be applied by almost all the known methods of dyeing. They are fairly simple to apply but not by any means foolproof; they should be stored under cool, dry conditions and kept covered, as they are likely to deteriorate if exposed to the atmosphere, although the stability of sulphur dyes is much better now than some years ago.

Dye vessels or machinery should be of stainless metal, wood, or iron. Brass or copper fittings should not be used, owing to the action of sodium sulphide on the metal. The dye is best dissolved by mixing it with soda ash and stirring into a smooth paste with water; sodium sulphide is added followed by boiling water, and boiling is continued with an open steam pipe for 10 min. When iron

vessels are used, a patina is formed on the surface of the metal by the action of the sodium sulphide, but it is normal for the shade to be flattened to some extent.

The solubility of the sulphur dyes varies appreciably, and adequate information on this point is usually given by the makers. The yellows require more sodium sulphide than other members of the range, but are not, as is usually supposed, the most insoluble; however, great care must be taken to ensure that a sufficient concentration of sodium sulphide is present in dissolving the dye, as it is impossible to obtain colour value from the dyebath otherwise. It is considered good practice to have a minimum of 2·5 g. sodium sulphide per litre in the dyebath.

Whilst considering the preparation of sulphur dyes, it is worth mentioning the possibility of using caustic soda and sodium hydrosulphite as a means of reduction— this idea is prompted by the desire to achieve as clean results as possible. Unfortunately, what appears to be feasible is not borne out in practice, as the degree of reduction appears to be excessive, and unless it is possible to establish optimum conditions, there is the danger that over-reduction will result in poor colour yield. Furthermore, the alkali–hydrosulphite bath is not so stable as sodium sulphide to oxidation. In some cases it also appears that dyeing from a hydrosulphite bath gives dyeings which have a lower fastness to washing than dyeings by the ordinary method.

It is of interest that, according to a report from the Mainkur I.G. Research Laboratory[1], the Germans made attempts to replace the sodium sulphide which normally is used in the dyeing of sulphur dyes by selected organic reducing agents. They evaluated for this purpose thioglycollic acid, thiosalicylic acid, and *pseudo*thiohydantoin. In many cases, it was found that these agents gave very good dyeing results, but for other sulphur dyes it was essential to have sodium sulphide present in the vat to obtain satisfactory affinity. Dyeings obtained from Immedial Direct Blue B with thioglycollic acid were reported to be particularly interesting because they were much redder than those from a normal sodium sulphide vat.

The foregoing shows that sulphur dyes have a wide field of application.

## Loose Cotton

There is good scope for the application of sulphur dyes to loose cotton, where colours reasonably fast to light and milling may be dyed, ultimately being mixed with wool and shoddy for the production of cheap suitings. The dyeing is usually carried out in open tanks or cisterns, where the material is poled by hand in the liquor— the subsequent processing of the cotton is such that any but serious cases of uneven dyeing are acceptable.

Recently the dyeing of sliver (which can be classed with loose cotton inasmuch as it is dyed before spinning) has been done on package machines, a very compact and effective way being to wrap the sliver round a perforated beam and carry out the dyeing in the same way as for cotton yarn on beam.

Machines of the Obermaier type may also be used for the processing of loose cotton, an advantage being that the yarn can be washed and hydro-extracted whilst in the same container.

## Yarn Dyeing

This includes the dyeing of cotton yarn in hank, cop, cone, cheese, and ball warp and on beam.

### HANK DYEING

The earliest and simplest method is that of dyeing in the open beck, where the yarn slung over sticks is turned by hand. The disadvantage of this method is the high labour cost, and also the fact that a portion of the yarn is out of the liquor and continually oxidising, unless specially shaped sticks are used to keep the yarn totally immersed in the reduced dye liquor.

Another difficulty arises in the washing-off, where the yarn is left saturated in dye liquor, which oxidises on the surface, so that when the yarn is washed the dye in the middle of the yarn, being still partly reduced and soluble, tends to wash off, giving uneven results. This has always been a serious problem in the beck dyeing of sulphur dyes, and it is interesting to note that in the *Manual of Dyeing*[2] it is suggested that a pair of squeeze rollers, similar to a household mangle, be mounted at the end of the beck, so that the yarn could be squeezed out of the dyebath before washing. Evidently labour cost was not such a formidable proposition then as now!

It is obvious that, apart from considerations of cost, the amount of yarn that can be dyed in one batch is limited, 100 lb. being about the maximum load. Other methods were adopted, and the Hussong machine is widely used. This machine consists of a wooden or stainless steel vessel fitted with a lid, underneath which is a rack fitted with sticks on which the yarn is suspended; the machine is fitted with a propeller which circulates the dye liquor. Some of these machines can dye up to 1000 lb. of yarn in one batch, and reasonably good results are obtained; i.e. results satisfactory for the purpose intended may be obtained, but if the yarn were intended for knitting, it is extremely doubtful whether the necessary degree of levelness could be attained.

Sulphur dyes may be applied on the Klauder-Weldon machine, but here again there is a great tendency to oxidation owing to the fact that the yarn is passing in and out of the liquor. The difficulty of achieving level results apart from the factor of oxidation is due also to the fact that sulphur dyes are in the main quick dyeing, and do not boil level. There are retarding agents which can be applied as in the case of vat dyes, but they do not appear to be as effective.

Yarn in hank form can also be dyed in package machines, some of the ordinary sulphur dyes being clean enough under well controlled conditions; this aspect will be referred to again in discussing the application of the water-soluble sulphur dyes.

### WARP DYEING

Warp dyeing will be taken throughout as relating to cross-ball or ball warp dyeing and not including beam dyeing. Cotton warps are used in a variety of trades such as cotton gaberdines (where both warp and weft are sulphur-dyed), union gaberdines (where the warp is worsted or woollen yarn and the weft cotton), flannelettes, ginghams, and tickings.

In warp dyeing both warp and weft may be dyed in warp form, the method being what is described as "open warp dyeing", where the warps are passed through multiple-box machines consisting of two, three, or more dye vessels fitted with guide rollers and squeeze rollers between each tank, with a final tank for washing.

The fundamental principle of warp dyeing where the dyed warp forms a solid shade is that the threads forming the weavers' beam are dyed as nearly as possible in the formation in which they will eventually appear on the weavers' beam. For example, if a cotton gaberdine cloth has 9600 ends or threads on the weavers' beam, 16 cross-ball warps of 600 ends up to 5000 yards in length can be dyed in one operation, care being taken that the relative positions of the threads remain unchanged once the dyeing operation has started (Fig. 1).

It will be seen that one big advantage of this method of dyeing is that enough warp yarn to make 50 pieces of cloth can be dyed in one batch; this in itself is not sufficient to recommend warp dyeing instead of piece dyeing, but another feature is the fact that a differently coloured weft is generally used, giving a "shot" effect, otherwise unobtainable in an all-cotton cloth.

To return to the dyeing operation, the warps are prepared for dyeing by passing through a boiling water bath, the dyeing process consisting in passing through the open warp machine; usually three or four runs are required to obtain the correct shade. To obtain level dyeing the amount of dye taken out of the dyebath should be replaced; various mechanical feeds have been tried, but in view of the fact that three or more dyes with different dyeing rates may be necessary to produce a shade, it has been found that a skilled operative is likely to produce the best results.

Another point to bear in mind is that, after the first run through a freshly charged dyebath, the end of the warps *last* out of the dye liquor is the *first* end through for the second run; by replenishing the dyebath, this end now has opportunity to "build up", thus giving some degree of equilibrium to the process. The first two runs are usually regarded as a means of getting the majority of the dye on level, and the third and fourth runs as a means of toning and matching the shade.

The dyeing of weft yarn in warp form is identical in principle, the only difference being certain adjustments in the manner in which the warps are run in order to conform with the conditions necessary for their subsequent winding. In general, weft dyed in warp form is processed in warps of 378 ends, so that they may be wound direct from warp to pirn on a machine containing 378 spindles.

The modification in processing is the doubling of the warps in such a manner that the yarn forming the beginning and end of the pirn passes through the dye liquor at the same time to avoid "weft bars" in cloth (Fig. 2).

The process of "open warp" dyeing is not usual outside this country, but from the foregoing description it will be seen that it represents an important section in the application of sulphur

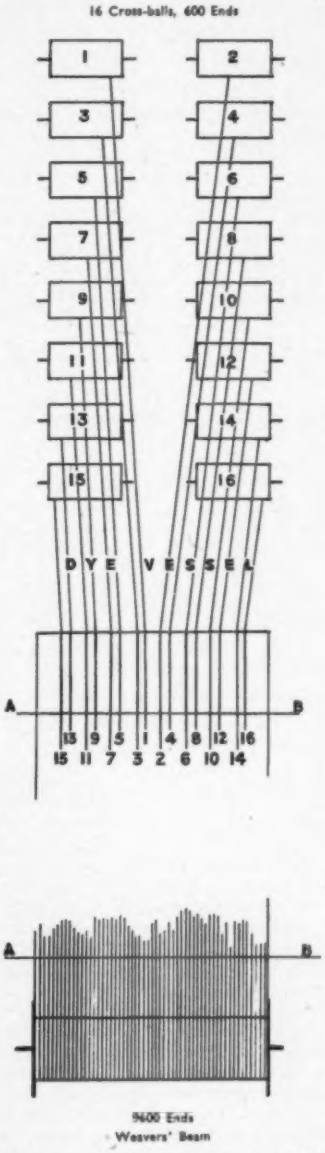



FIG. 1—Maintenance during Warp Dyeing of the Relative Positions of Warp Threads on the Weavers' Beam to ensure Levelness

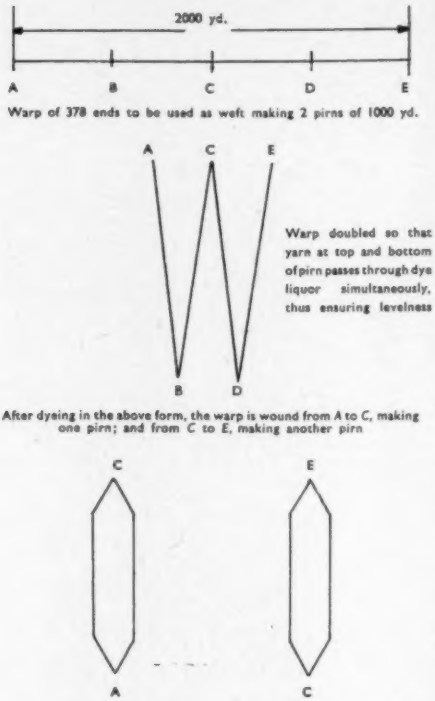

2000 yd.
A
B
C
D
E
Warp of 378 ends to be used as weft making 2 pirns of 1000 yd.
A
C
E
B
D
Warp doubled so that yarn at top and bottom of pirn passes through dye liquor simultaneously, thus ensuring levelness
After dyeing in the above form, the warp is wound from A to C, making one pirn; and from C to E, making another pirn
C
E
A
C

FIG. 2— Dyeing Weft in Warp Form

dyes. In the light of this it is appropriate to consider the aftertreatment of such dyeings, which can be taken as representative of sulphur dyeings in general.

After the preparation and dyeing of the warps as described above, it is usual to finish through a seven- or eight-box machine by treating with sodium dichromate and acetic acid, then washing well with running water, and finally soaping at 120–140°F. This treatment with sodium dichromate is important, as it provides a chemical oxidation to as permanent a stage as possible; this gives a more reliable basis for repetition matching, as sulphur dyeings if finished only by washing and soaping "age" further after drying, and sometimes change considerably over a period of time. This is general with sulphur dyeings, the extreme cases being certain prune and corinth shades, which are susceptible to alkaline fumes and should be finished with a rinse in acetic acid.

### COP, CONE, CHEESE, AND BEAM DYEING

In the three processes described above— namely the dyeing of loose cotton, cotton yarn in hank, and cotton yarn in warp— the material is dyed under conditions where any slight uncleanliness is no serious detriment, as the liquor ratio and method of dyeing do not tend to cause precipitation on the material, in contrast to machines where the liquor is circulated through the material, which thus acts as a filter.

The other sections of yarn dyeing referred to are all essentially processes where the dye liquor is circulated through the package. Machines may be adapted for circulating the liquor in one direction, e.g. from inside to outside, or it may be circulated alternately "in to out" and "out to in".

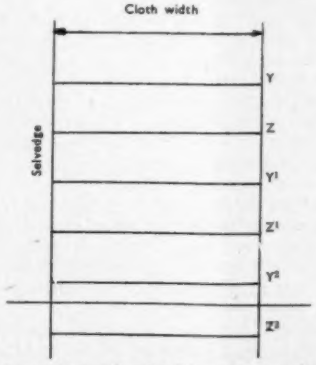
The range of ordinary sulphur dyes contains members which, if carefully applied, give satisfactory results in cop, cone, cheese, or beam dyeing, and it is indeed a remarkable achievement that sulphur dyes have progressed to this stage, where they can be applied by such an exacting method. It is one of the biggest developments in the application of sulphur dyes, although the standard reached in pressure dyeing may not be entirely suitable for all purposes.

## Soluble Sulphur Dyes

It is no doubt this factor of cleanliness which has led dyemakers to strive for dyes in the sulphur range which are clean and easy of application— in short, colours which can be applied in all types of machines, thus removing all objections that sulphur dyes are unsuitable for certain purposes on the grounds of unsuitability of the dye as distinct from any lack of fastness. This led to the introduction of the Immedial Leuco (IG) dyes before the war.

These dyes were water-soluble owing to the fact that the dyes had been converted to their leuco compounds, but not apparently by the use of sodium sulphide. These dyes were undoubtedly readily soluble, but on account of their cost were suitable only for specialised purposes. Furthermore, they were not very stable in storage, which also militated against their use.

The next big development was the introduction of the water-soluble sulphur dyes, which have the property of dissolving in water without the addition of sodium sulphide or alkali, but it must be emphasised that this aqueous solution will *not* dye cotton. The addition of soda ash and sodium sulphide is necessary to convert the dissolved dye into a condition possessing affinity for cellulose.




Assuming one pirn weaves from Y to Z, any variation in shade between C and A (Fig. 2) would show a bar at each cop change

FIG. 3— How the Method of Dyeing ensures the Same Shade at Top and Base of Pirn

The property of being water-soluble has several advantages— it enables stock solutions to be made, thus giving closer control of repetition recipes and also of feeding liquors. In the case of package dyeing, the aqueous solution can be circulated through the material and later reduced, when the dye is developed *in situ*, thus giving very level results.

This has a big advantage over dyeing in package machines with reduce ' dyes, as in the latter case the portion of the material which receives the first impact of the dye liquor is bound to be slightly darker than the opposite side of the package. This is extremely important if we consider a type of work such as gaberdine weft, where absolute levelness is essential. Under present conditions the general practice is for the weft to be dyed in warp form as described above, and then to be wound on to pirn, where the length wound is rigidly controlled to conform with the method of dyeing.

Even with the greatest possible control (consistent with works processing) it is not by any means possible to guarantee a perfect result. In order to emphasise the degree of levelness required, let us imagine a dyeing in warp form where the warp consists of 378 ends, which are then wound on to 378 separate pirns. These pirns are then woven into cloth, where we can assume that each pirn will weave less than one foot of cloth; therefore, unless every pirn is identical in depth and hue at the beginning and end, some weft barriness of varying degree will be caused, producing a Venetian-blind effect, which is very detrimental and can, in fact, render the cloth unsalable (Fig. 3).

Thus dyeing for this purpose is a very difficult procedure, and the same applies to union gaberdines, where the warp is worsted. This means that, unless the weft is perfectly level, a tremendous liability can be incurred by the processor, owing to the high value of the resultant product. Without introducing commercial considerations, it is not inappropriate to consider the question of liability in commission processing in view of the rapidly increasing cost of raw materials, namely cotton and wool. As a result it is vital that every precaution in processing must be taken to ensure a first-class result, even if only in self-defence. Surely, then, the prospect of processing yarn in package form for gaberdine weft by means of water-soluble sulphur dyes could in one operation solve many dyeing problems, particularly in achieving levelness. This also would allow the winding process to be reorganised to give large packages such as cones, which could later be wound by machinery of the single-end type, without regard to length, producing a pirn comparable with the type used in weaving grey cloth, thus giving greater efficiency in weaving. Here is a further vital point where production can be improved, and it does not seem unreasonable to relate industrial progress in manufacturing to increased efficiency in dyeing brought about by improved dyes giving advantages in application, which lead to a general improvement in all stages of manufacture, in both quality and methods of processing. This would make the use of water-soluble sulphur dyes justifiable on grounds of quality alone, but the structure of commission processing is such that the operation should be satisfactory both technically and economically. This means that, if by evolution of better dyes and technique of application, better results and methods of manufacture are achieved, then the operation should be regarded as vertical, and the dyer should be adequately rewarded for his efforts.

It is interesting to note, in connection with sulphur dyes of the readily soluble or water-soluble types, that the Swiss produced some dyes known as Eclipsols which were more stable than the Immedial Leuco dyes, but they could not be applied at temperatures much lower than the boil, as the reducing agent employed did not become effective below that temperature. These dyes are not being produced now.

Dyes are now being produced in Germany under the name Immedialsols (CFM*). These products are dry preparations consisting of sulphur dyes, sodium carbonate, and Rongalite C as reducing agent, which is added to the sulphur dye paste before drying in order to obtain a final product which, it is claimed, will produce level dyeings, and which will dissolve instantly in the dyebath. A special "dyeing assistant" is recommended for addition to the dyebath, and this is believed to consist of Rongalite and soda ash. These dyes may also be applied with the addition of ammonia and sodium hydrosulphite to the dyebath. Varying quantities of Rongalite are used in the preparation of different members of the range, presumably to conform with the best conditions for reduction of the dyes concerned. The following are typical examples[1]—

Immedialsol Black 9

| Parts | |
|---|---|
| 50 | Immedial Brilliant Black G |
| 25 | Rongalite C |
| 24·5 | Soda ash |
| 0·5 | Oil |

Immedialsol Bordeaux B

| | |
|---|---|
| 24·9 | Immedial Bordeaux G |
| 24·9 | Rongalite C |
| 49·7 | Soda ash |
| 0·5 | Oil |

Immedialsol Blue 5G

| | |
|---|---|
| 19·8 | Immedial Green Blue CV extra |
| 19·8 | Rongalite C |
| 39·6 | Soda ash |
| 9·9 | Sodium sulphate (anhydrous) |
| 9·9 | Sodium metasilicate |
| 1·0 | Oil |

It is reported that dyes containing sodium sulphide are not suitable for this Rongalite process, as hydrogen sulphide is evolved.

It is evident that this technique in manufacture and application of sulphur dyes is becoming increasingly important. Messrs. James Robinson & Co. Ltd. have produced sulphur dyes in paste form which are dyed by the method given below; this seems to be a further pronounced step in making the package dyeing of sulphur dyes a straightforward operation.

The dye is readily dissolved in hot water (180°F.) and diluted to a working volume, in this case 10 : 1 liquor in a pack machine with one-way circulation. Calsolene Oil HS (ICI) (3 g./litre) was added to the liquor, which was then circulated for 1 hr. at the

* Cassella Farbwerke Mainkur

boil. At this stage the sodium sulphide solution is added, and the dyeing carried on for a further 15 min. at the boil. An addition of 20% common salt is then made in two portions with an interval of 15 min. The dyeing is concluded after a total dyeing time of 90 min., and the yarn is well rinsed in hot water and aftertreated with sodium dichromate and acetic acid.

The two dyes used were a cutch brown and a prune; dyeings of the individual dyes were made, and also a dyeing of the two dyes together, which was level, especially considering the contrasting tones of the component dyes.

The method used in demonstrating levelness is to prepare "pad wrappings" of a continuous length of yarn (which in these trials was in hank form) by the method evolved by the British Cotton Industry Research Association for assessing the levelness of dyed mercerised yarns, which exaggerates any unevenness.

Sulphur dyes of the water-soluble type may be applied to wool–cotton and wool–Fibro union yarns by the following method—

The amount of sodium sulphide is reduced to one-half, and the soda ash replaced by sodium bicarbonate to the extent of three-quarters of the amount of sodium bicarbonate as dye. The maximum temperature of dyeing should not exceed 170°F. The dye is pasted with warm water, and boiling water added (if necessary the solution may be boiled, but *not* after the sodium sulphide and sodium bicarbonate have been added).

The prepared dye liquor is then raised to 150°F., and dyeing carried on for 60–75 min., when 15–30% common salt is added, and the dyeing finished during a further hour.

The yarn is then well rinsed, hydroextracted, and treated with dichromate and acetic acid; a final good rinsing and soaping are then given. The degree of staining of the wool varies with each dye. Some sulphur dyes give almost solid shades, whilst others give good reserve of the wool. Yarns dyed by this method are suitable for the wool to be dyed in a separate bath with level-dyeing acid or chrome dyes.

The foregoing covers the developments in the range, scope, variety, and fastness of sulphur dyes, and the vast improvement in the technique of their application. Whilst this paper is confined to the application of sulphur dyes to yarn, it is not an unreasonable speculation to wonder whether, with suitable methods of reduction, it may not be possible to apply them by the molten-metal process developed for vat dyes.

In conclusion, some reference ought to be made to the question of the tendering of cotton yarn dyed with sulphur dyes, particularly sulphur blacks. This tendering occurs on prolonged storage, particularly when the cloth had been subjected to acid cross-dyeing. Some preventive treatments are recommended, including the aftertreatment of the yarn with bichrome to form and remove the oxidation products before the material is stored. Also, treatment with sodium bicarbonate or sodium acetate minimises the risk of tendering on storage.

Whether the condition of the dye influences the issue is debatable, but in the writer's experience cases of sulphur black tendering do not seem to occur as frequently as some years ago; however, whether the conditions of storage have improved or whether the material dyed is no longer stored for such a length of time owing to the present state of supply and demand is not certain.

### References

[1] *FIAT* 1313 (London: H. M. Stationery Office), **3**, 252–257.

[2] Knecht, Rawson, and Loewenthal, *Manual of Dyeing* (London 1893).

## Discussion

Mr. S. BURGESS: The author has referred mainly to the dyeing of cotton with sulphur dyes, but they are also of great interest for dyeing viscose rayon, not so much for continuous filament as for staple fibre. They are much cheaper than vat dyes (although not always very cheap), and are especially useful in attempting to match heavy shades on wool.

With reference to the "intelligent selection" of sulphur dyes, whilst there are many different factors to take into account, such as fastness, price, type of dyebath, leuco or otherwise, one wonders whether the Society should not eventually attempt some classification of the sulphur dyes, possibly according to methods of application and other dyeing properties. Something on these lines has been done at Droylsden[3]. From solubilities given on some dyemakers' pattern cards, it is immediately obvious that it is not always possible to dye in the lowest attainable liquor : goods ratios. We at Droylsden have been obliged to dye in longer liquor ratios in order to have enough sodium sulphide solution to dissolve the dyes.

The package dyeing experiment undertaken in collaboration with Messrs James Robinson & Co. Ltd. is in line with work done in the vat dye field. If it were possible to dye otherwise incompatible dyes together in this or some similar fashion, this would represent a considerable step forward in the application of sulphur dyes.

Mr. BIRCHALL: In so far as "intelligent selection" of sulphur dyes is concerned, it may be said that the overriding principle is similar to the dictum of Dr. Whittaker with reference to direct dyes, viz. "common salt and common sense". The main points to observe are adequate amounts of sodium sulphide to maintain the dyebath in good condition and adequate solubility of the dyes used, both in the dyebath in short liquor ratios for package dyeing and in the feed liquors used for warp dyeing.

Mr. T. FLANAGAN: The author states that the Thionol M brands can be circulated through the package and later reduced, when the dye is developed *in situ*, thus giving level results. Does

[3] Whittaker, C. M., and Wilcock, C. C., "Dyeing with Coal-tar Dyestuffs" (London: Baillière, Tindall & Cox. 5th edition 1949), p. 246.

the author imply a padding technique similar to the Abbot–Cox process, and has he any evidence that the dye, in aqueous solution, can be transferred from the dyebath to the yarn before reduction?

Mr. BIRCHALL: In applying the water-soluble Thionol M brands by circulating the aqueous solution, there is no reason to believe that the aqueous solution can be exhausted on to the fibre. It is reasonable to believe that, when the material is impregnated with the dye solution, it will be uniformly penetrated with substantive liquor when the dyebath is reduced, the risk of unlevelness which can be produced by the impact of a reduced liquor on the undyed yarn thus being avoided. Results show a higher degree of levelness from the Thionol M brands than from the orthodox method of dyeing from a reduced dyebath.

Mr. FLANAGAN: The Immedialsols seem to have been dismissed in this paper with only a passing reference. I have applied these dyes to viscose rayon cakes in an open type of circulating machine, and have found that they are stable and yield much more level results than those obtained using the conventional sulphur dyes, which require sodium sulphide for reduction. The yarn after dyeing has quite a soft handle, whereas it has been my experience that normal sulphur dyes impart a harsh handle. Does the author think that dyes of this nature, where Rongalite C is used as the reducing agent instead of sodium sulphide, would be of assistance in overcoming some of the difficulties encountered in package dyeing?

Mr. BIRCHALL: Comment on the Immedialsol brands is restricted owing to limited experience, but there is no doubt whatever that dyes where Rongalite C is used as reducing agent should find wide application especially in package dyeing, particularly if other advantages accrue such as the improvement in handle described by Mr. Flanagan.

Dr. R. L. ELLIOTT: The last paragraph of the paper states that Sulphur Black tendering is not now so frequent as in the past. A recent case of excessive tendering occurred in a store of Sulphur-Black-dyed yarns, sewing threads, and linings of raincoats. Is there any suitable treatment which would satisfactorily prevent this trouble?

Mr. BIRCHALL: The statement in the paper refers only to the experience of the author. Various methods of aftertreating cotton yarn have been suggested, the chief being a treatment with dichromate with a view to producing the undesirable acid-forming oxidation products as quickly as possible; it is important that this should be followed by efficient rinsing. Another method is to aftertreat the yarn with sodium acetate, leaving it slightly alkaline. Neither method is completely effective, but it must be borne in mind that the yarn may form the weft of a cloth with a woollen or worsted warp which is later cross-dyed, so that the cotton may be left in an acid condition, resulting in tendering which is not in any way due to the Sulphur Black.

Mr. H. HAMPSON: Could Dr. Elliott say what the linings were made from? In thirty years' experience I have never known of a complaint of tendering of viscose rayon dyed with Sulphur Black.

Dr. ELLIOTT: The linings were all-cotton material, and the outer material was a cotton warp–worsted weft gaberdine; all sewing threads were of linen or cotton. No rayon was involved in any materials used in the raincoats concerned.

Dr. C. M. WHITTAKER: In the case of tendering quoted by Dr. Elliott I would suggest that the conditions of storing may well play an important part, seeing that the garments were not made from the dyeing of one dyehouse. Gas heating of the warehouse is one possible cause.

Mr. H. E. BREW: If the outer fabric was oil-proofed, the degradation of the linings could perhaps have arisen from the product of oil oxidation under the conditions of storage rather than from Sulphur Black tendering.

Mr. J. HOLT: With the necessity to develop and improve methods of continuous production, it would be interesting to hear the author's views on the future regarding the dyeing of sulphur dyes. Does he visualise that development will take place in warp dyeing and beam dyeing, or will continuous processing methods, such as the Standfast machine, replace the older, more conventional methods?

Mr. BIRCHALL: Whilst some schools of thought would abolish sulphur dyes altogether in favour of vat dyes, it is evident, on grounds of cost alone, that sulphur dyes will maintain a place in the scheme of things. Developments such as the water-soluble and Immedialsol types will provide for package dyeing in all its forms, and, if suitable methods of reduction are discovered, it is feasible that sulphur dyes may be applied by the Standfast molten metal method.

Mr. S. EMMOTT: The oxidation of dyed cones or cheeses in pressure machines is usually effected in the first place by vacuum extraction. As dyeing proceeds during extraction, unevenness is caused. The alternative is to wash, involving excessive loss of dye. What does the author recommend?

Mr. BIRCHALL: It is by no means certain that dyeing proceeds during extraction, as results show that cops, cheeses, or cones, if *immediately* extracted from the dyebath, give level results. The use of oxidising agents such as dichromates would tend to cause precipitation of oxidised particles on the inside of the package.

Mr. C. P. ATKINSON: The question of tendering referred to was also a matter of great concern in the past, the fault being normally accentuated when cotton lining fabrics dyed with Sulphur Black were subjected to the tailor's ironing procedure. It appears to be a matter of reflection on some of us that Dr. Elliott has to refer to the same problem some thirty-five years later. Should not this matter be the subject of investigation by some of our Research Associations?

Mr. BIRCHALL*: Considerable work has been done on the investigation of the tendering of yarns dyed with Sulphur Black.

* Communicated

# Developments in the Azoic Dyeing of Yarns

W. THORNBER

A brief account is given of the history of azoic dyeing, from the discovery of Vacanceine Red by Read Holliday Ltd. in 1880 up to the present day.

Azoic dyes are insoluble azo dyes which have no direct affinity for vegetable fibres, but are produced by impregnating the material with a "naphthol" and coupling with a diazotised base or salt, thus producing a coloured lake or pigment on the material.

A very large range of shades can be produced, e.g. yellows, oranges, scarlets, reds, maroons, browns, blues, and blacks. Many of these have good fastness to washing, boiling soda, bleaching, light, etc., and the dyer, when matching a shade, should take great care to use the combination which will give him the required fastness.

Azoic dye components have been available from 1912 under the trade-name of Naphtols (IG), but were first discovered in the year 1880 by the firm of Read Holliday, their chief dye being Vacanceine Red, made from $\beta$-naphthol and $\beta$-naphthylamine. The name Vacanceine probably came from the French word *vacances*, which means "holidays", but most of those who dye azoic dyes will agree that they are far from being a holiday.

Vacanceine Red offered a cheaper and simpler method of obtaining a fast red on cotton than Alizarin or Turkey Red, and achieved considerable success. Other examples of insoluble azo dyes, such as Para Red, $\alpha$-Naphthylamine Claret, Benzidine Puce, Dianisidine Blue, Chloranisidine Scarlet, etc., quickly followed on, and were widely used, the best of them being Para Red and Dianisidine Blue. They were very important up to the time of the modern azoics, but are now of minor importance, and find practically no use for the dyeing of yarns, though it appears that they are used in certain calico printing styles.

This older group of insoluble azo dyes were not very fast; colour would stain off on to the white along with which they were woven, even when dyed under the best of dyeing conditions, and soaping aftertreatments would not eliminate this staining. They were, however, much faster than the direct dyes to washing, and had a reasonable fastness to light. Rubbing fastness was their worst factor.

The Holliday patent of 1880 was thus described as the first practical application of the idea that insoluble azo dyes might be produced on vegetable fibres.

Weber, Galland, and von Gallois subsequently improved the process, but the Holliday patent contains the germ idea of the so-called "ice dyes", up to the time when the Griesheim-Elektron Co. introduced Naphtol AS in 1912, and named the combinations with diazotised amines *azoic* dyes.

After the first World War, the azoics made very rapid progress, and within a few years there was practically a complete range of colours for the dyer's use. Progress was also made in the technique of dissolving the naphthols and diazotising the colour bases, so that they were considerably more stable both in the dyebath and in the stock bath. Some of my first experiences with the azoics involved difficulty in bringing some of the naphthols into solution. When diazotising some of the colour bases a tarry substance formed on the top of the liquor; this had first to be removed very carefully, and then the whole of the stock liquor had to be sieved at least twice before use. Ice was used in abundance to keep down the temperature, and even after all our care, the developing baths would sometimes go out of condition and thus spoil our work by giving flat and uneven shades.

At the present time nearly all the principal dyemaking firms manufacture azoic dye components, which are sold under various trade names such as the following— Brenthols (ICI), Naphtols (NCO), Cibanaphtols (Ciba), Irganaphtols (Gy), and a few others.

Corresponding products in each of these ranges are, of course, chemically identical, and below are a few examples of the hues produced by corresponding Naphtols in conjunction with various Bases.

| Brenthol (ICI) | Naphtol (NCO) | Hues produced |
|---|---|---|
| AS | AS | Orange, scarlet, red, and blue |
| CT | AS–TR | Reds and maroons of good bleaching fastness |
| AN | AS–BO | Wines and maroons |
| FO | AS–BG | Red and tans of good light fastness |
| FR | AS–OL | Bright oranges and reds |
| MA | AS–LT | Reds and maroons of good light fastness |
| PA | AS–RL | Reds and maroons of good light fastness |
| AT | AS–G | Fast-to-bleaching golds, etc. |
| BT | AS–LB | Browns, fast to light and bleaching |
| DA | AS–BR | Red-browns |
| RB | AS–SR | Black with Fast Red B |

There are a few brands of naphthols on the market which are soluble in boiling water, and are claimed to require no addition to the bath, which is therefore very easy to prepare. The Solunaptols marketed by John W. Leitch & Co. Ltd. are examples of these brands. These products are weaker than the normal type, and appear to be mixtures of the naphthol with a dispersing agent and an alkaline compound.

There are numerous Bases on the market, both I.C.I. and Naphtol-Chemie A.-G. (NCO) using the same names and brand marks in general, except that the former firm uses the prefix "Brentamine". The following are examples—

Brentamine Fast Red GL Base or Salt (ICI)
Fast Red GL Base or Salt (NCO)

We can now say a little about the practical side, chiefly about the dyeing of cotton yarns mainly in the form of chain warps.

Azoics at the present time give us a very large range of most excellent colours in pleasing shades of very good all-round fastness properties.

The dyeing process consists essentially of three stages— impregnation, development, and soaping — each of which will be considered in turn.

### IMPREGNATION

Impregnation with naphthol solution can be carried out on various types of machines, e.g.—

CHAIN WARPS are dyed in the continuous warp box machine, where the warps are impregnated and developed at one run through. The circulating-liquor machine can also be used for warps.

HANK YARN is dyed in the circulating-liquor machine or by the tub liquoring process, also in the open beck or box.

COPS, CHEESES, AND LOOSE COTTON are dyed in the circulating-liquor machine.

The depth of shade obtained depends upon the amount of naphthol taken up by the fibre, which is governed by the following factors—

(*a*) The concentration of the solution
(*b*) Affinity or substantivity of the naphthol for the cotton
(*c*) The length of time given for impregnation
(*d*) Liquor ratio (the lower the liquor ratio the higher the proportion of naphthol absorbed).

#### *The Azoic Warp-dyeing Machine*

At the first view, this machine appears to be a conglomeration of dye tanks, squeezers, and rollers; one might call it a glorified mangle. In truth, it is very substantial and quite capable of dyeing large weights of cotton warps.

The machine is 60 ft. long, made up by connecting together seven dye tanks or boxes. The first two boxes are smaller than the rest, having a working liquor capacity of 50 gal. each, and are used for the naphthols. We apply most naphthols hot, and the warps must be cooled before developing. This is done by running over rollers in the air before passing into the developing box, which is lined with stainless steel and holds 200 gal. The rest of the boxes are of cast iron, hold 300 gal. each, and are used for cold and hot water washing off, etc.

All rollers are of stainless steel; the squeezers are rubber-covered, and are capable of giving a very good squeeze.

The dyeing is a continuous process, whereby the impregnation with naphthol, developing, and washing are done in one run through, after which the soaping treatment is carried out on another machine.

When the machine is in operation, the dry warps pass through the hot naphthol, are squeezed twice, pass over rollers in the air to cool down, are squeezed again, pass into the developing bath, are squeezed again, and continue through the wash waters.

After dyeing and washing, the soaping is carried out on another 60-ft. machine made up on similar lines to the dyeing machine. All the seven boxes are the same size and hold 300 gal. of liquor each; five boxes are charged up with 3 g. soap, 1 g. Lissapol N (ICI), and 2 g. soda ash per litre, and the other boxes contain boiling water.

Both the dyeing and soaping machines run at a speed of 1000 yd. per hour and are capable of dyeing up to 1500 lb. weight in one lot or run of warps. When dyeing the standard red shade, and providing there is enough weight of yarn, the baths can be worked for several days, and "feeding on" is carried out while the machine is in operation.

#### *Dyeing of Standard Red with Brenthol FR and Fast Red RC Base on 1000 lb. of Warp Yarns*

Prepare the machine with—

| | | |
|---|---|---|
| 14 lb. | ... | Brenthol FR |
| 14 pints | ... | Turkey Red Oil 40% |
| 17½ pints | ... | Caustic soda (62° Tw.) |
| 28 gal. | ... | Boiling water |

and boil until clear. This solution is divided into the two naphthol boxes, being first prepared with Turkey Red Oil and caustic soda, and made up to 50 gal. each at 180°F.

The feed required has the same composition; it is boiled until clear, and made up to 80 gal. with cold water.

DEVELOPMENT— Fast Red RC Base (18 lb.) is pasted up with 18 pints of hot water; to this is added 18 gal. cold water containing 14½ pints hydrochloric acid (32°Tw.), and 9½ lb. sodium nitrite dissolved in 4½ gal. cold water is added whilst stirring vigorously. After standing for 30 min. at 55°F. with occasional stirring, the excess hydrochloric acid is neutralised by the addition of about 14 lb. sodium acetate dissolved in 4½ gal. cold water; the alkali-binding agent required is 7 pints of acetic acid (50%). The solution is then diluted up to 40 gal. with cold water; 5 pints of Azopol A and 30 lb. common salt are added, and the developing solution is now ready for use.

The developing box is prepared with cold water, 6 lb. Base, i.e. one-third of the above solution, and 45 lb. common salt (30 g./litre) are added, and made up to 150 gal. with more cold water, when the temperature should not be above 55°F. To the rest of the developing solution (12 lb. Base) another 5 pints of acetic acid is added, and this is used for feeding.

Feeding liquors are added into the machine whilst the yarn is running, the shade being dyed at one run through; for further 1000-lb. lots the feed required would be 14 lb. Brenthol FR and 12 lb. Fast Red RC Base for each lot.

When dyeing smaller lots of 350–600 lb. yarn in other shades, it is more economical to dye on the two-run method, i.e. by giving the warps two runs through the dyeing machine to obtain the shade, instead of one run; this gives a great saving of naphthol, and also a saving of colour base, as the baths are more exhausted. The use of common salt where possible is also a great advantage.

Warp weights up to 350 lb. are more satisfactorily dyed by giving the naphthol impregnation

in circulating-liquor machines, and then developing through the two-box warp machine as follows. The warps are packed into stainless steel containers which have been lined first with white or grey cotton cloth, then put into the circulating-liquor machine, which has been prepared with the required amount of naphthol, etc. at the correct temperature, and circulated for 20–40 min., well hydroextracted, and run out of the container through the two-box warp machines prepared with the colour base, etc. in the first box and running cold water in the second box, after which soaping is carried out.

Standing baths can be used when more than one dyeing is wanted, by feeding on with naphthol for each lot, and feeding on with colour base in the developing machine.

Azoic yellow and gold shades dyed with Brenthol AT are far better dyed on the circulating-liquor machine, as this Brenthol is applied cold; the penetration is unsatisfactory when dyed on the open warp machine, and after repeated washings the undyed fibres inside the yarn begin to show through, thus giving the cloth a very skittery appearance. The following is a recipe for a standard gold shade, fast to piece bleaching for the tablecloth trade—

Weight of yarn ... 600 lb.
Dyed in two lots of 300 lb. each, starting with a new bath and feeding up for lot No. 2.

Prepare—

| | | |
|---|---|---|
| 15 lb. | ... | Brenthol AT |
| 12 pints | ... | Turkey Red Oil |
| 25 pints | ... | Caustic soda (62° Tw.) |
| 22 gal. | ... | Boiling water |

boil for a few minutes until a clear solution is obtained.

The machine, which holds 250 gal. of liquor, is prepared by adding—

| | | |
|---|---|---|
| 3 pints | ... | Turkey Red Oil |
| 5 pints | ... | Caustic soda |
| 10 lb. ... | ... | Brenthol AT solution |
| 45 lb. ... | ... | Common salt |

the rest of the Brenthol solution is used for feeding on the second lot.

The container with 300 lb. of warp yarn is put into the machine and circulated for 40 min. at 60°F., then hydroextracted well, and passed through the two-box warp machine prepared and fed as follows—

Fast Orange GR Base (10 lb.) is mixed to a paste with 12 gal. cold water, and 5 lb. 10 oz. sodium nitrite added. When the nitrite is dissolved, add quickly whilst stirring into 18 pints of hydrochloric acid in 30 gal. cold water; after standing for 20 min. at 50–60°F. with occasional stirring, the excess hydrochloric acid is neutralised by the addition of 13 lb. sodium acetate, and the required alkali-binding agent would be about 10 pints of acetic acid. Then add 20 lb. common salt. The machine is prepared with 100 gal. cold water at 50–60°F. and 30 lb. common salt. Two-fifths of the above solution (4 lb. of Base) is used in the first box, and running cold water in the second box.

The rest of the developing solution (6 lb.) is fed on while the warps are passing through the machine. After dyeing, soaping is carried out by the usual method.

It is important that no formaldehyde should be added to the Brenthol AT bath, as the colour-producing properties of the Brenthol would thereby be destroyed.

### PREPARATION OF THE NAPHTHOLS

The naphthols are insoluble in water, and it is necessary to form the soluble sodium salt of the naphthol at the time of dissolving as follows—

Paste up the naphthol with the required amount of a good dispersing or wetting agent, e.g. Turkey Red Oil, Azomel A, etc., then add the required amount of boiling water, keep boiling and stir in the required amount of caustic soda, and continue boiling until a clear solution has been obtained.

It is most essential that the naphthol solutions are quite clear and correct in condition, or a very poor dyeing would be the result, e.g. poor fastness to rubbing and bleeding off on to adjacent white material during subsequent wet processing of the goods.

The dyebath is made up to the required volume of water at the working temperature, and then the additions of the dispersing or wetting agent and caustic soda are made before the concentrated naphthol solution is added. This helps in maintaining the clear solution which is so necessary.

Some modifications are used, however, in the cases of Brenthols GR, DA, GB, and RB.

#### *Recipe for Brenthol AS*

Brenthol AS (1 lb.) is pasted with the wetting agent, and 1½ gal. boiling water added; while boiling 1¼ pints caustic soda (60°Tw.) is added, and the solution boiled until clear.

This solution is cooled down to 120°F. by the addition of about 1½ gal. cold water, about ¾ pint formaldehyde (40%) being added if required; the solution is diluted to the required volume containing the necessary additional amounts of wetting agent and caustic soda.

Naphthols vary in the amounts of wetting agent, caustic soda, and water required, and for the best results the recipe required for the particular naphthol should be used, as given by the makers. Standing baths can be used, and in doing so there is a considerable saving of naphthol; the correct feeding quantities must be used if standing baths are to be properly maintained, and they vary considerably for each naphthol, but these can be determined with accuracy from the absorption tables published by the makers.

After impregnation, the material must be thoroughly hydroextracted or squeezed, as the fastness of the subsequent shade largely depends upon it. Insufficiently hydroextracted or squeezed material will give rise to the formation of a loosely held pigment, which cannot be properly cleared afterwards.

The yarn is now ready for stage No. 2, that is development.

### DEVELOPMENT

The developing baths are made up by using the Fast Bases or Salts. Fast Salts are easy to use, as they dissolve in warm water, whereas the Fast Bases have to be prepared by being subjected to a diazotisation process, which converts them into soluble diazo compounds giving solutions like those of the Fast Salts.

The following is the procedure with Brentamine Fast Red KB Base—

The Base (1 lb.) is pasted with 1 gal. hot water containing 0·8 pint hydrochloric acid (32°Tw.). Mix well, making sure that all lumps are broken down. Dilute the solution with 2½ gal. cold water to a temperature of 50–60°F., and then add slowly a solution of 6½ oz. sodium nitrite dissolved in 2 pints cold water, whilst stirring vigorously. Allow this to stand for 20–30 min., giving an occasional stir, and then add a solution of 12 oz. sodium acetate to remove excess hydrochloric acid. Add ½ pint acetic acid (50%) as the alkali-binding agent. Here, again, the individual diazotisation recipes for the colour bases should be referred to. (Diazotisation is best carried out in wooden or earthenware vessels.)

Alkali-binding agents are used to neutralise the caustic soda which is carried by the material into the developing baths. Alkali tends to inhibit coupling and is the cause of decomposition of the diazo compound; it thus causes uneven, dull, and not very fast shades. There are various alkali-binding agents, e.g. acetic acid, sodium bicarbonate, aluminium sulphate, sodium acetate crystals, etc., the use of which must be in accordance with the recipe for the Base being used.

The diazotised Brentamine Fast Base is now ready for use in the developing bath. This bath, for general purposes, is preferably maintained at temperatures not exceeding 60°F., and an addition of common salt up to 25 g./litre is made in most cases. The salt prevents the naphthol from being removed from the fibre before it has been fully developed. Exceptions are as follows—

The common salt addition is reduced to 10 g./litre in the cases of—

Brentamine Fast Garnet GBC Salt or Base
Brentamine Fast Corinth V Salt

The common salt is omitted from the baths prepared from—

Brentamine Fast Red AL Salt
Brentamine Fast Black K Salt

in order to avoid precipitating soluble constituents.

YELLOW SHADES FROM BRENTHOL AT—The developing baths require to be more strongly acid than is the normal case, and in order to avoid dull and uneven results an addition of 3·5 c.c./litre (3 pints per 100 gal. of acetic acid (50%)) is therefore made. This amount is additional to the quantity of alkali-binding agent normally present. In general a Brentamine Fast Base dyebath should react faintly acid to litmus paper.

The addition of Azopol A to the developing baths increases stability, results in a better dispersion of the diazo solution of the Brentamine Fast Bases and Salts, and thus helps to obtain cleaner dyeings. Azopol A will cause the unfixed colour pigment that is formed during the development stage to be maintained in a state of colloidal solution. This loose colour pigment is thereby prevented from being precipitated on to the dyed material, or if any pigment does remain on the material after developing, it is easily removed by the subsequent rinsing and soaping, etc. The use of Azopol A gives a marked improvement in the fastness, and the developing bath can be used for a much longer time. When the material has been passed through the developing bath and is fully developed, it is essential to give a rinse in cold water, followed by soaping for 30 min. at the boil in a solution containing 3 g. soap and 2 g. soda ash per litre.

The use of Lissapol LS (ICI) gives very good results, especially with hard water, and the amount required is about 1·5 g. Lissapol LS and 2 g. soda ash per litre.

In the case of chain warps, it is impossible to soap for 30 min., and as warps are usually dyed in the length and generally done in large (approx. 1000-lb.) lots, the soaping must be carried out in the same type of machine as they are dyed in, but with much larger boxes so as to give a longer liquor. Some of these machines have up to 8 or 10 boxes fitted with top and bottom rollers, and have squeezing rollers between each pair of boxes, thus giving 8–10 squeezes. These boxes are charged up with soap, soda ash, and sometimes a good dispersing agent. The warps are run through, and the machine man must feed on soap and soda continually whilst the machine is running. Sometimes the warps have to have more than one run through to ensure sufficient soaping. After soaping, the warps are given a good rinse in hot water.

The soaping treatment is a very essential part of the dyeing process, as it removes the mechanically adhering colour pigment, thus ensuring that good fastness to rubbing is obtained. Soaping also develops the true hue, and by means of a good soaping we get the maximum fastness to washing, chlorine, and light. Certain combinations should only be soaped at 150°F., or a dull shade will be obtained.

It may be mentioned here that the use of common salt in some of the naphthol baths helps to give faster and also cheaper dyeings.

Azoic dyes are used in the dyeing of yarns for a great variety of cloths and fabrics, including the following—

POPLINS, where fastness to bleaching and Trubenising is required.

GINGHAMS, NURSE-CLOTHS, REGATTAS, ETC., where fastness to severe and repeated washing is required.

CASEMENT AND FURNISHING FABRICS, where very good fastness to light is required.

In view of the fastness requirements of the above cloths, it is important that the azoic dyeings should be carried out correctly, and therefore care has to be taken that the naphthol and developing

baths are used in correct condition, as otherwise the resultant dyeings would be faulty. In addition the importance of giving a satisfactory finishing to the dyed yarns, in order to attain the necessary fastness to rubbing and washing, etc., must be stressed.

In conclusion it may be said that very few modern ranges of fast coloured articles can be regarded as complete without employing azoic-dyed yarns, and the modern demand for brightness of shade and high fastness would be a long way from fulfilment without these dyes.

## Discussion

Mr. F. Smith: Has the author any experience of either the mixing of two naphthols or coupling with two or more Bases? Is it better to mix the former or the latter?

Mr. Thornber: It is much better to mix naphthols than Bases. The former mix well and dye level shades; whereas with the Bases, uneven dyeings are more likely to result. Fastness to light is often impaired by the mixing of either.

Mr. F. Crompton: Has the author as much difficulty in dyeing dianisidine on yarns as the printer has in printing it?

Mr. Thornber: I have had no experience with the printing of Dianisidine Blue, and cannot compare the two.

Mr. F. Crompton: Has the author much trouble with tar deposits in $\alpha$-naphthylamine claret dyeing on $\beta$-naphthol?

Mr. Thornber: Tar deposits constituted a great source of trouble when dyeing $\alpha$-naphthylamine claret (great care must be taken in keeping the temperature down to 32°F. with ice; also the liquor must be very well sieved before use). This combination is out of date for yarn dyeing, as there are better azoic combinations to choose from, of superior all-round fastness and with no tar deposits at all.

Mr. T. Flanagan: In dealing with the factors which govern the amount of naphthol taken up by the fibre, the author has omitted to mention temperature. This is a very important factor in viscose cake dyeing, where even impregnation of the yarn can be obtained only by commencing the impregnation at a fairly high temperature and dyeing in a cooling bath to promote exhaustion.

Mr. Thornber: Naphthols go on to cotton warps very evenly when on the package machine. There is therefore no need for temperature control other than working at the temperature recommended for the naphthol in use. I agree that temperature control is important when dyeing rayon yarns.

Mr. Flanagan: The author recommends (and apparently practises) hydroextraction of the naphtholated yarn before coupling, even when package dyeing. This is a very big disadvantage, involving unloading of the machine and subsequent repacking. Apart from the alkaline–saline rinse technique, can the author suggest or recommend any other procedure which would eliminate this hydroextraction?

Mr. Thornber: Faster results are obtained by hydroextraction between the naphthol and developing baths. This can be done with warps, as we then run from the container through the developer, which is in the open warp box machine. I can recommend no methods other than hydroextraction, vacuum, and the alkaline-saline wash of the naphtholated yarn before developing.

Dr. E. R. Trotman: With reference to the production of azoic dyes on cheeses, is not trouble experienced with unlevel distribution of precipitated dye due to filtration difficulties? There is a view quite commonly held that azoic dyes cannot be used in package dyeing. Can yarn in hank form be dyed successfully in the Obermaier type of machine?

Mr. Thornber: A fair amount of package dyeing (e.g. of cones, cops, cheeses, and cakes) is done at the present day with success. Great care must be taken through the various stages of the dyeing, developing, and soaping processes—

(1) Naphthols must be dissolved well, and the use of Azomel in place of Turkey Red oil is recommended, as this gives a better solution.

(2) Bases should be correctly diazotised, and used at the temperature stated. The use of Azopol A or Diazopon A keeps down precipitation in the developing process.

(3) "Soaping off" is better if done by the use of such agents as Lissapol, Teepol, etc., as one is then sure of the material being free from lime soaps.

(4) Hanks can be dyed on the package machine, or one may naphtholate on this type of machine, then extract off, develop on the open box, wash, and soap in the usual manner.

Mr. E. E. Bowker: An addition of formaldehyde to the naphthol solution to act as a stabiliser against the action of light and atmospheric conditions is usual practice when impregnation is carried out at low temperatures. Such an addition would cause precipitation of the naphthol solution at high temperatures, and it would be of interest to know the author's experience of the stability of the naphthols in the absence of formaldehyde when exposed to light and atmospheric influences, particularly after impregnating on the Obermaier type of machine, where repacking after hydroextraction means that considerable time elapses before development takes place.

Mr. Thornber: I quite agree that, when formaldehyde is used, the temperature of the naphthols must be kept down when the time between the two operations is considerable. But when naphtholation and development form a continuous process (as in warp dyeing), high temperatures can be used, and hence shades much faster to bleeding and rubbing are obtained. When dyeing warps or hanks on the package machine, the best temperature is that recommended for the naphthol being used, and formaldehyde is then used with most naphthols.

Mr. S. Burgess: The author has envisaged the use of azoic dyes for casement and furnishing fabrics, the life of which often must be very long.

I have always felt that only the few very good azoic combinations should be used for casements, and only in shades of maximum depth, which are least likely to fade. Dr. C. M. Whittaker has on many occasions pointed out that, when azoics do fade, they tend to fade out completely. Does the author agree with this policy, or would he extend the use of azoics to other combinations?

Mr. THORNBER: We can say that there are some dyes which last as long as the garment, e.g. some vat and azoic dyeings with respect to washing fastness. I agree that there are very few, if any, which are fast to light for the full life of a curtain. At the present day one has to use combinations which give the best results. The light fastness must not be under 7.

Mr. BURGESS: It appears that the author has adhered to the orthodox approach of securing fastness to rubbing by careful attention to detail at every stage of the process and final treatments with soap or other detergents and sodium carbonate at high temperatures combined with adequate mechanical treatment. We have had difficulties in securing azoics fast to rubbing, and have had many suggestions offered to us, from using no soap at all to using very high concentrations of soap and also treatments with such substances as oil emulsions. Has the author any knowledge of these or other unusual suggestions being in any way consistently successful?

Mr. THORNBER: The best results for soaping off azoic dyeings are obtained by using a very high liquor ratio. An extra tank can be coupled to the package machine, and the liquor then circulated one way (in to out), letting the dirty soap liquor run out through an overflow at the top of the machine. Detergents such as Teepol, Lissapol N, etc. can be used, and have been found to be of advantage on various occasions.

Mr. L. MORRIS: The cold dissolving method for naphthols has a certain usefulness for (*a*) forming clear impregnating liquors and (*b*) keeping alkali-binding power constant in the developing beck. Can the author say whether there is available any solvent other than industrial spirit, free from excise restrictions, which may be used for this process?

Mr. THORNBER: I know of no other solvent which is free from excise restrictions.

Mr. W. PENN*: The author has stressed how important is the soaping operation in obtaining satisfactory fastness to rubbing. This operation, which consists of alternate soaping and squeezing treatments, is perfectly satisfactory for cotton. What modifications are needed in order to avoid damage to rayon staple warps, bearing in mind that rayon staple is more susceptible to mechanical damage than cotton whilst in the wet state?

Mr. THORNBER: Rayon warps are best dyed by (*a*) naphtholating on the package machine, and (*b*) developing by running through the open box machine. Then wash, repack the warps, wash again on the package machine, and then soap off in a soap bath of high liquor ratio. Synthetic detergents can be used instead of soap. Very good results are obtained by this method of working.

* Communicated

# Developments in the Dyeing of Piece Goods with Vat Dyes

D. Haworth and W. Kilby

The trend in the development of the application of vat dyes to piece goods has been outlined. Whilst a survey of the whole field has been made, so far as is possible from the published literature, particular attention has been paid to the difficulties encountered in developing the Standfast molten-metal machine as a bulk production unit.

Although vat dyes were introduced some fifty years ago, the methods of application to fabrics remained substantially unchanged until comparatively recent times.

In the fabric-dyeing process, the dye was usually applied on the jig and the time of application was of the order of one hour. Steps were taken, for example by the use of retarding agents, to slow down the rate of transfer of dye from liquor to cloth, so as to achieve maximum uniformity of shade and penetration.

In the printing process, the dye, together with British Gum or other thickening, and the various reducing chemicals were applied to the cloth, and the resultant print after drying was subjected to an atmosphere of moist steam for a period of the order of ten minutes. The fact that reduction and fixation could be achieved in this shorter time was due to the increased rate of solution and absorption at the higher temperature and the restriction of the movement of the dyes away from the sites where fixation was required. In an alternative printing process thickened vat dye was printed and dried, and the reducing chemicals were applied in a padder immediately before steaming. An increased rate of fixation and shorter steaming resulted from the larger amount of moisture in the steamed fabric and the higher reaction rate of the reducing chemical used.

In dyeing practice, the nearest approach to printing technique was the so-called pigment-padding process, where the vat dye was applied on the pad as a suspension of unreduced dye. Again fixation was achieved by application of the reducing chemicals on the jig, and with such a discontinuous process utilising large amounts of liquor it was necessary to use conventional temperatures with lower rates of fixation.

The problem of evolving a system for the continuous application of vat dyes exercised a considerable amount of thought among dyers and technicians. The desiderata of a continuous dyeing process have been fully elaborated by Boardman [1] and others. In order that an objective study can be made of the various techniques which have been developed, a brief résumé is tabulated below.

A satisfactory process should eliminate or at least minimise the following disadvantages inherent in jig dyeing—

1. Atmospheric oxidation effects
2. Stains due to sewing repeats, etc.
3. Stained batch ends
4. Difficulty of getting perfect matching from batch to batch
5. Difficulty of predetermining results
6. Restriction of choice of dye combinations
7. Difference of affinity in mixed fabrics.

Also the process should possess the following characteristics—

(*a*) Economy of processing in chemicals, steam, and labour.
(*b*) Ease of changing from one shade to another.
(*c*) The process should be able to handle large outputs at high speed, and at the same time it should be possible to handle small lots economically.
(*d*) The quality of work must be at least as good as, and preferably better than, that dyed by any other method.
(*e*) It must be possible to handle satisfactorily widely varying qualities of cloth in any depth of dyeing.
(*f*) The speed of running should not influence the shade.
(*g*) The feed liquor should have the same composition as the dyebath.
(*h*) It must be possible to dye the full range of vat dyes either singly or in combination with each other.
(*i*) The dye liquor or booster liquor should be held at high temperatures for only a brief period.
(*j*) The process should be mechanised, so that it calls for little technical skill on the part of the operator.

## REDUCED PAD DYEING

Probably the earliest method of continuous dyeing was reduced pad dyeing. Dry cloth was padded with the reduced vat dye solution, and passed directly into open-width washing boxes for rinsing, oxidising, and soaping. Owing to the limited time between impregnating and rinsing, the dyes show poor penetration and cannot achieve good fixation. Hence colour fastness is poor, and the method is limited to pastel shades.

## LIQUID BOOSTER BOXES

A logical development of the above was the introduction of liquid booster boxes. In this process, the cloth, after passing through the padder containing reduced dye solution, passes directly into one or two large tanks or boosters. These "booster" baths contain caustic soda, sodium hydrosulphite, and sufficient reduced dye to establish dye equilibrium between the bath and the fabric passing through. The goods are then washed, oxidised, and soaped.

The function of the boosters in this process is to ensure that adequate time is allowed for the reduced dye to achieve penetration and fixation. To ensure uniformity of shade from beginning to end, there must be a dye equilibrium between booster liquor and fabric. The necessary control requires skill and experience, since in the dyeing of combination shades the varying affinities of the dyes for the fibre necessitate careful adjustment of the feed.

There are, however, some limitations to this process. Firstly, it is not possible to dye dark shades, because the maximum concentration of dye

in the padding box is determined by the solubility of the leuco compound. Secondly, since the usual capacity of the booster baths is of the order of 1500 gal. of solution, considerable quantities of dyes and chemicals are required to set the baths at the beginning of the run. Therefore long yardages are essential for the economical operation of this process.

The reduced-pad liquid "booster" was satisfactory up to a point, but the logical development of this method lay in the direction of finding a technique that would permit the full development and fixation of pigment-padded cloth (so that any depth of shade could be handled) and could also effectively reduce the volume of the booster baths.

### WILLIAMS UNIT[2]

This unit, which has been fully described in American technical literature, represents an improvement over the older continuous dyeing techniques. By the design of the machine and the arrangement of the baffles and heaters, the effective volume of the unit is decreased to about 70 gal., giving a liquid : cloth ratio much smaller than in the older processes. A high temperature is maintained, and this gives rapid fixation of the dyes.

The strength of the reducing liquor is maintained by constant controlled additions of caustic soda and hydrosulphite. It is recommended that the hydrosulphite be fed dry to the unit. When used for developing pigment-padded fabric, it is essential that dye be added to the developing liquor at the beginning of the run, in order that equilibrium shall be speedily established between fabric and liquor. Oxidation and soaping are carried out either in further Williams units or on conventional ranges.

Although the volume of liquor is much smaller than in the early methods, difficulties are encountered owing to the varying dyeing rates of the different vat dyes, and the correct concentration of dye in the pad and the unit are very important.

The Williams unit may be used as a straight dyeing unit containing the reduced dye, as a booster for the treatment of fabric which has been padded in reduced dye, or finally as a developing unit for wet or dry pigment-padded fabric.

A suggested set-up for an all-purpose Williams-unit continuous vat range is given by General Dyestuff Corpn. as follows—

1 Padder
1 Hot-flue drier
2 Williams units for reduction (piped together)
1 Williams unit for cold rinsing
1 Williams unit for oxidation
1 Williams unit for hot rinsing
1 Williams unit for soaping
1 Williams unit for hot rinsing
1 Drying range

SHADE MATCHING is carried out on a laboratory model of the unit. It is considered essential for successful matching that use is made of the physical forces of speed and the turbulence of the dye liquors, caused by passing the cloth through the narrow passages of the unit at high speed.

### PAD–STEAM PROCESS (DU PONT)

This process can be considered to be a logical outcome of the study of printing technique. The considerable reduction in the time of fixation is due mainly to the absence of thickening and the increased moisture content of the cloth during steaming. This facilitates the rapid solution of dye particles and transfer of dye to the fabric. The basic process is as follows—

Pigment pad and dry
Chemical pad with cold caustic soda, sodium hydrosulphite, and salt (to minimise bleeding)
The impregnated cloth is then passed into an atmosphere of air-free moist steam, which gives full reduction and fixation in 15–30 sec.
The cloth then passes to a conventional range for oxidation and soaping.

The process operates most efficiently when handling large runs, but it is stated that runs of the order of 1000–2000 yd. can be handled.

There are several variations of technique possible with the pad–steam process, which can be tabulated briefly as follows—

1. Pigment pad— dry— chemical pad— steam, etc.
2. Pigment pad— chemical pad— steam, etc. This method is used on unmercerised cloths, especially if loosely woven.
3. Pad reduced— steam, etc. Used only for light shades.
4. Pad acid vat— do not dry— chemical pad— steam, etc.

4(*a*). Acid vat— dry— chemical pad— steam, etc.

Methods 4 and 4(*a*) are suitable only for light shades, and considerable manipulative skill is required for the production of the correct acid vat.

5. Pigment pad— chemical pad— steam and liquid boosters, etc.

SHADE MATCHING is normally done either on a laboratory padder designed to give the same expression as the bulk padder or preferably on the production padder. Development is then carried out in the laboratory steamer, and if done correctly the method can be fairly reliable. It can, however, easily become unreliable as a shade-matching technique.

### STANDFAST MOLTEN-METAL MACHINE[3]

As the result of intensive research carried out at Standfast Dyers & Printers in Lancaster since 1945, fusible metals were successfully applied to a process of continuous vat dyeing, and bulk-scale machinery was put into production at the Lancaster works.

At a meeting of the Manchester Section of the Society, Boardman[1] fully described the process. The essential feature of the machine is an iron U tube having two legs each 5 ft. deep and about 1 in. thick. The cloth passes in open width through the dye liquor, which floats on the upper surface of one arm of the U tube, down this arm, and then up the other, giving a passage through the metal of a little over 10 ft.

This brief description covers the essential features of the machine itself, but the various mechanical and electrical devices necessary to obtain maximum control in the use of the machine as a continuous dyeing unit require some elaboration.

The Standfast process is unique in that the padding mangle is eliminated as an essential component of the equipment. The molten metal provides at one and the same time a padding mechanism, a heat transfer medium to permit rapid fixation of dye, and a seal to ensure complete exclusion of air, which facilitates reduction and fixation.

The molten metal, owing to its characteristics as a fluid, exerts equal pressure from all directions on a point below its surface. It can also modify the surface applying pressure according to the nature of the surface requiring pressure; thus in the processing of cloths in which the thickness shows great variation, the metal adapts itself to these variations and gives a constant proportion of liquor per unit weight of cloth.

The liquor : cloth ratio averages 1·4 : 1 depending on yarn and cloth construction. The metal is a very efficient heating medium and is in close contact with the fabric, giving rapid heat transfer. Thus there exist a metal temperature of 95–105°C., a very short liquor ratio, and complete exclusion of air. Because under these conditions there is a rapid transfer of leuco dye from dye liquor to fabric, it is possible to apply all vat dyes by this process. In fact, experimental combinations of Caledon Red BN, Caledon Blue RN, and Caledon Yellow GN (ICI) have produced excellent results when applied by the Standfast process.

During the adaptation of this basically simple idea to the successful processing of bulk runs, several difficulties occurred which had to be overcome to achieve complete success. It is now proposed to outline some of these problems and their solution. These notes are not necessarily in the chronological order in which the difficulties were encountered.

It was observed during the early trials that streaks developed on the cloth in the direction of the warp, these varying from paler shades of the true shade down to almost white. Their appearance suggested that dye liquor was being scraped from the cloth before fixation could be achieved. The various ways in which this might happen were investigated, and it was realised that solidification of the surface of the molten metal could well cause this defect. This solidification could be caused by the feeding of cold cloth to the dyebath.

The cloth was therefore preheated by passing it over steam-heated cylinders before feeding it into the dyebath. It was also found that when high metal temperatures were used (110°C. upwards) steam was generated at lower parts of the metal bath and passed upwards through the dyebath, causing imperfect contact of fabric and dye liquor.

It is essential that the cloth enters the metal centrally to minimise the possibility of its coming into contact with the walls of the machine (see below). To effect this, guide rails are formed on the sides of the dyebath, and these orient the cloth so that it is in fact delivered in a central position to the metal bath.

As mentioned before, it is essential to prevent the cloth from coming into contact with any flat surfaces during its passage through the metal. Once contact has been made, there is a considerable pressure due to the metal, rising to 20 lb./sq. in. at the bottom of the machine. This pressure tends to maintain contact between the cloth and the sides of the machine, and a very considerable force is necessary to overcome it. To eliminate this difficulty, the faces of the walls of the machine are serrated by grooves, which are triangular in section, being about $\frac{1}{4}$ in. deep, and $\frac{1}{4}$ in. wide at their base. This simple expedient very effectively prevents this trouble; without the grooving, it would be difficult even to thread an end cloth through a narrow slit machine.

The most difficult problem encountered in the early days was the formation of a sulphide scum at the metal surfaces, which led to heavy loss of alloy and affected levelness of dyeing. This was caused by the decomposition of the hydrosulphite, and the extent of formation was influenced very considerably by several factors in the process. The most notable of these were the length of time the reduced liquor was maintained at a high temperature (this also affected the stability of the dyes themselves), the concentration of chemicals in the dye liquor, and the condition of the bath on the exit side of the machine.

It is interesting to correlate the time required for sulphide formation with the temperature of a caustic hydrosulphite solution. At room temperature, using a mixture of 30 g. Hydros (Br) and 20 g. caustic soda per litre, there was no evidence of sulphide formation after 8 hr. (a normal working shift). At higher temperatures, the length of time taken for sulphide formation to develop decreased rapidly. Thus at 95°C. sulphide was detected within 5 min.

It became essential to devise a method of reducing the time of maintaining the hydrosulphite–dye liquors at high temperatures. To effect this, the dye liquor was made up to the required volume with dye, caustic alkali, hydrosulphite, and the necessary wetting and dispersing agents. The mixture was stored cold, and on its way to the dyebath was pumped through a very efficient heater, which quickly raised its temperature to the required level.

No attempt was made to obtain complete reduction and solution during the making up of the dye liquor, and the normal vatting procedure was omitted. At room temperature the hydrosulphite and dyes are reasonably stable for some hours. Reduction occurs in a few seconds during heating in the passage of the dye liquor to the dyebath and through the molten metal, this being possible with the finely dispersed modern vat dyes (see below).

Several vat dyes are unstable in alkaline hydrosulphite solutions if maintained at temperatures above 60°C. for long periods. With the concentrations of chemicals used in the Standfast process, with certain vat dyes (principally those of the Caledon Blue RC type), some degradation is apparent after 20 min. at 60°C. The delayed heating of the dye liquor therefore eliminates this degradation as well as the scum formation.

During the investigations on the formation of sulphides in aqueous alkaline hydrosulphite liquors it was found that abnormally high concentrations of caustic soda (e.g. 100 g./litre) accelerated the rate of formation. Compounds such as formaldehyde, Rongalite (IG), hexamine, and sodium thiosulphate had a similar effect. On the other hand, a number of compounds retarded the formation of sulphides, and the most effective of these was found to be glucose. Thus addition of 15 g. glucose per litre to a solution of 30 g. Hydros and 20 g. caustic soda per litre at 95°c. lengthened the time interval before sulphide formation could be detected from 5 to 10 min. Investigation showed that the optimum quantity of glucose was half the weight of hydrosulphite, though in practice a figure of 15 g./litre is not exceeded for reasons of expense, the extra protection achieved above this figure not warranting the additional cost.

It is essential that the fabric emerges from the molten metal through a hot wash liquor, to prevent the carry-over of metal alloy. Originally a solution of ammonium sulphate was used to fulfil this function, but a solution of Glauber's salt was found to be more satisfactory, and this is now used. It is necessary to heat such a rinsing liquor to a temperature above the melting point of the alloy, and since it becomes contaminated by alkali and hydrosulphite washed from the fabric, it would tend to have a stripping effect in the absence of salt. Acidic conditions in this exit liquor must be avoided because of increased rate of sulphide formation in acidic hydrosulphite liquors.

Considerable trouble was caused at one time by the formation of an oily scum in the oxidising bath. This was due to the breakdown of the wetting agents used (after being in contact with the reducing liquor) and the formation of chrome complexes with these degradation products. This problem was overcome by the investigation of a range of available wetting agents and the selection of those which were satisfactory in all respects.

Circulation of Dye Liquor— At 30 yd./min. the cloth is immersed for 0·44 sec. in the dyebath; at 120 yd./min. the cloth is in the dyebath for only 0·11 sec. Bearing in mind these short times of immersion, it is extremely important that the dye liquor is uniform in concentration, because any variation would show in the finished product. This uniformity is achieved by feeding the dye liquor into the dyebath through gallery pipes extending the whole length of the dyebath on both sides of the cloth and situated below the surface of the liquor.

It was found that, in spite of this method of feeding, a certain amount of stagnation occurs at the ends of the dyebath, even though the cloth causes considerable agitation of the dye liquor in a vertical plane. To overcome this stagnation and maintain uniformity, the dye liquor is now circulated in the bath. This circulating system is entirely separate from the dyebath feed. A horizontal as well as a vertical movement of the liquor on both sides of the cloth is induced. Complete uniformity both in dyebath composition and in finished products is achieved by a total flow of 6 gal./min.

Shade matching is carried out on a laboratory machine which is adjusted to run at such a speed that the time of immersion in the metal is the same as in the bulk machine. After the shades have been matched, the bulk dye liquor is made up, and as a final precautionary measure a further sample of this is run through the small machine. Once this check has been made satisfactorily, the bulk run can be made without any trial pieces.

When details of the Standfast process were released in March 1950, Imperial Chemical Industries Ltd. considered it essential that an independent first-hand study of the method should be made. To achieve this, a laboratory scale model of the machine was constructed.

This machine, although basically the same as the laboratory checking machines in use at Standfast, varies somewhat in refinement. The metal alloy container is immersed in a boiling water bath, and dye liquor is fed by gravity through a coil also immersed in the water jacket. The cloth is preheated by radiant heat units on its way to the dyebath. The machine has a variable-speed drive, so that it is possible to vary the time of immersion in the molten metal.

Speke[4] states that, as a preliminary to the investigation of the factors affecting the application of vat dyes to cotton by the Standfast molten-metal process, experiments were undertaken to determine the most effective ratio of sodium hydrosulphite and sodium hydroxide in the feed liquor. It was deduced from theoretical considerations that when the $Na_2S_2O_4$ : NaOH ratio was 2, the maximum reducing power should be realised without any danger of acidity developing in the feed liquor. Experiments confirmed that this was the most effective ratio, although varying it between 2 : 1 and 1 : 1 produced no difference of a major order.

Using this ratio of 2, the relation between the dye content and the reducing agent concentration was then determined for four dyes of widely different properties when applied by conventional means. The dyes used were—

Caledon Red Violet 2RN
Caledon Brown R
Caledon Blue RC
Caledon Jade Green XN

and feed liquors were prepared containing 150 g. single-strength dye per litre. The experiments listed in Table I were then carried out.

Table I

| Experiment | Sodium Hydroxide (g./litre) | Sodium Hydrosulphite (g./litre) |
|---|---|---|
| 1 | 2·5 | 5 |
| 2 | 5 | 10 |
| 3 | 10 | 20 |
| 4 | 25 | 50 |

Shades of equal colour value and fastness properties to those obtained by traditional methods, in the case of all four dyes, were achieved by using the concentrations in Experiment 3.

Variations in reducing agent sensitivity were noted from dye to dye. In all four experiments, Caledon Jade Green XN gave the same result. Caledon Brown R and Red Violet 2RN gave no fixation with the concentrations in Experiment 1,

and only moderate fixation with those in Experiment 2. Caledon Blue RC gave little or no colour yield in Experiments 1 and 2.

It was apparent, however, that a set of conditions could be established whereby all types of dye could be applied with equal facility. Similar experiments, undertaken over a wide range of dye concentration, established a relation between the dye and the reducing agent concentrations which is constant irrespective of the classification of the dyes by conventional methods.

By interpolating in the graphs obtained by plotting the results of these experiments, Speke compared the consumption of reducing agents, based on the dry weight of cloth, for any given depth of shade in jig dyeing, the pad–steam process, and the molten-metal process. Table II gives the percentages of reducing chemicals, based on the dry weight of cloth, required for the production of a 10% dyeing of single-strength dye.

TABLE II

| | Jig | Pad–Steam | Molten Metal |
|---|---|---|---|
| NaOH (%) ... | 2–3 | 3–3·5 | 0·75 |
| $Na_2S_2O_4$ (%) ... | 3–5 | 3–3·5 | 1·5 |

EFFECT OF DYE QUALITY— Particle size has no effect on the quality of production by the molten-metal process. Thus, dyeings of equal colour value and fastness are obtained irrespective of whether dyes of pigment-padding or dyeing quality are used.

These results confirm conclusions reached as a result of bulk operation of the Standfast machine.

The molten-metal continuous vat dyeing process is capable of handling economically runs of any yardage, and the change-over time between successive shades averages about 5 min. At the time of going to press, about 17,000,000 yd. of vat-dyed fabric, in a wide variety of shades and on a wide range of cloths, has been produced.

### WILLIAMS UNIT–HOT OIL PROCESS[5]

A recent development which has been publicised in the American press is the Williams unit–hot oil process. In this technique, cloth is pigment-padded and then, with or without intermediate drying, passed into a Williams unit containing caustic alkali and hydrosulphite at 80°F. as reducing liquor. The fabric then passes into a further Williams unit containing a selected mineral oil at 215°F. At this temperature, rapid fixation of the dye takes place, and the time taken for complete fixation is said to be 10–12 sec.

After passing through the hot oil, the cloth passes into a cold bath of Igepal CA, which disperses the oil carried over, so that it can be removed in the scouring bath. It is stated that there is no contamination of the oil, and that a yellow can follow a royal blue without affecting the shade.

The carry-over of oil by a 6-oz. cloth is about 1 gal. per 150 yd. or about 1300 gal. per week on a weekly yardage of 200,000.

The oxidation and soaping can be carried out in either Williams units or standard open-width machines. The hot oil fulfils the same function in this process as does the steamer in the pad–steam process.

### VAT-CRAFT DYEING PROCESS[6]

A report of this process states that fabrics are impregnated with a solution of materials, which when exposed to radiation are converted to insoluble coloured pigments. To speed up the reaction a radioactive uranium isotope UA 1 is added to the dye solution.

In this process the fabric is passed through the dye solution containing the radioactive catalyst, nipped, then passed through a shallow pan containing a photosensitising solution, and nipped again. The fabric then passes to the development chamber, which contains two banks of fifteen lights covered by screens of 96% silica glass. These lights produce 112·5 kw., and it is claimed that when the fabric leaves this chamber the colour is completely fixed.

The fabric then passes through water to remove lint, dirt, etc., and then on to conventional finishing ranges.

According to reports the users are prepared to accept orders of a minimum yardage of 5000, and work on dark shades is not as advanced as on light and medium shades.

### CELLULOSE ETHERS AS DYE CARRIERS[7]

Information has been published recently about a new American process in which cellulose ethers are used as dye "carriers". In this process, which was communicated by Dan River Mills Inc., the cellulose ether is dyed as raw stock with vat dyes, oxidised, and soaped. The pre-dyed cellulose ether, after dissolving in alkali, is precipitated on the cloth to be dyed, by souring with acid.

The amount of subject-matter relevant to this paper is so vast that it has been impossible to do more than outline the major developments in a logical sequence. No attempt has been made to present a critical account of any of the various methods or processes, the emphasis having been laid where possible on the practical aspects of developments in the dyeing of piece goods with vat dyes.

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[3] Morton Sundour Fabrics Ltd., Hannay, R. S. E., and Kilby, W., *B.P.* 620,584.
[4] Speke, R. W., Lecture delivered at Gothenburg to the Swedish Technical Dyers Association (16th April 1951).
[5] General Dyestuff Corpn., *Technical Bulletine* Ex 175 E, etc.
[6] Vat-Craft Corpn., *Amer. Dyestuff Rep.*, **38**, 960 (1949).
[7] Abbey, A., *B.P.* 649,140.


## Discussion

Mr. E. H. MATTINSON: Does the Standfast molten metal method process enable sulphur dyes to be continuously dyed, in view of the possibility of the formation of sulphide scum?

Mr. HAWORTH: Certain of the water-soluble Thionol M (ICI) brands have been applied satisfactorily in bulk runs.

Mr. MATTINSON: Has the molten metal method

any application in the vat dyeing of such fibres as nylon or Terylene, i.e. fibres which are difficult to dye?

Mr. HAWORTH: We have not had an opportunity of doing any bulk experimental work on these fibres, and prefer not to comment until such work has been done.

Mr. F. CROMPTON: Will the author give us some information on the grooves necessary to stop the cloth from rubbing on the sides of the machine?

Mr. HAWORTH: The grooves in the walls of the molten-metal machine are triangular in section and about $\frac{1}{4}$ in. deep and $\frac{1}{4}$ in. wide at the base of the triangle. They function by forming troughs of metal between the cloth and the walls of the machine (thus reducing the area of contact should this occur), and also maintain a uniform pressure on both sides of the cloth. Thus, should contact occur, the force required to break it is very considerably reduced, and no undue tension is imposed on the cloth.

Mr. CROMPTON: Has the machine been used with ferrous sulphate and caustic soda or lime instead of Hydros?

Mr. HAWORTH: All bulk processing of vat dyes has been carried out with caustic soda and sodium hydrosulphite.

Mr. M. R. FOX: A limited number of experiments with the ferrous sulphate–caustic soda vat have been made at Blackley using Caledon (ICI) dyes. Results have not been very satisfactory, however, and this can probably be associated with the low rate of reduction and incomplete vatting obtainable from these assistants.

Dr. H. W. SCHEFFERS: Is not the time of immersion in the dyebath itself less important than the time in the molten metal?

Mr. HAWORTH: The time of immersion in the dyebath is important only in so far as it provides complete wetting and mechanical impregnation of the cloth by the dye liquor. Once complete wetting has been achieved, further immersion is unnecessary and in some cases can be undesirable. No attempt is made to achieve dyeing in the dyebath itself.

Dr. SCHEFFERS: How does the fastness of the dyeings compare with those obtained by other processes?

Mr. HAWORTH: Tests carried out on dyeings by the molten metal process give fastnesses at least as good as those obtained by any other process of applying vat dyes.

Dr. SCHEFFERS: What types of wetting agents are suitable for the molten metal process?

Mr. HAWORTH: Most wetting agents can be used. The choice will vary according to the particular fabric being processed.

Mr. K. LOWIT: Can Mr. Haworth tell us about the machine he used for the fixing of vat prints?

Mr. HAWORTH: Considerable laboratory work has been done in this direction, and the results show great promise. Until we have had an opportunity of doing some bulk experimental work, however, we do not wish to make any definite claims to the trade.

Mr. M. R. FOX*: In speaking of the effect of dye quality the authors may be unwittingly conveying an erroneous impression by stating that "particle size has no effect on the quality of production by the molten metal process". Presumably they are specifically referring to the use of the modern finely dispersed Powder Fine and Paste Fine qualities of dyes, which are capable of giving fine aqueous suspensions and which are free from large aggregates commonly referred to as "cobs". Obviously, large aggregates of incompletely reduced dye, which are liable to arise from the use of imperfect dispersions, would be deposited on the cloth during dyeing. In the Standfast machine, these particles would have insufficient time to become fully reduced and levelled out in the short metal contact periods employed. This state of affairs would therefore result in specky dyeings.

Experiments at Blackley have confirmed that dyes of the Powder Fine, FD Powder Fine, and Paste Fine brands showing comparatively wide variations in particle size show no significant differences in the ultimate excellent quality of the dyeing or in the colour yield when using the Standfast technique.

Mr. A. S. FERN: What are the relative merits of hot oil and molten metal as a developing medium for vat dyes?

Mr. HAWORTH: Until we have an opportunity of examining production by the hot oil process, we cannot make any comments on its merits.

Mr. FERN: Have the authors studied the penetration of molten metal into fabrics and fibres? How far can such properties as density, viscosity, and surface tension be used to predict how far and in what way the molten metal (or hot oil) penetrates the cloth?

Mr. HAWORTH: No.

Mr. S. PEARSON: In view of the short contact time between cloth and metal, is it feasible to apply vat dyes to cellulose acetate from the normal alkaline vat without serious saponification occurring? If so, what is the possibility of obtaining a solid shade on, say, an acetate–viscose rayon mixture fabric?

Mr. HAWORTH: Vat dyes have been satisfactorily applied in laboratory machines to cellulose acetate from the normal alkaline vat, without the use of swelling agents and with little or no saponification of the acetate. Results obtained on viscose–acetate rayon fabrics vary with the dyes used.

Mr. W. PENN*: The operation of dyeing cannot be divorced from preceding processes such as desizing and scouring, and it would appear that high-speed methods of preparation are necessary in conjunction with high-speed continuous dyeing processes. Rayon staple fabrics may present a problem as regards high-speed continuous preparation.

Mr. HAWORTH*: We have little or no information to communicate about high-speed continuous preparation.

* Communicated

# Progress of Package Dyeing with Vat Dyes and Indigosols

FRED SMITH

Hot-dyeing vat dyes strike on to the fibre very quickly even at low temperatures. With open-beck dyeing on hanks, small lots only could be dyed with any success. On cotton in hank or on properly wound cones, cheeses, or beams, package dyeing enables the dyer to put the dye liquor where it is required more quickly and more evenly and produce a good result without the use of retarding or levelling agents. Should there be any slight fault in the build of the package, faulty dyeing will be the result. Higher temperatures up to 200°F., with dyes that will stand them, will sometimes overcome these faults. It is safer to use a suitable retarding agent from the start. The same remarks apply to the dyes of Classes B and C that strike very quickly.

The introduction of stainless steel machines has led to greater use of the package system.

Large weights of cotton yarn are now dyed in one batch with vat dyes, up to 2000 lb. suitable for casements, denims, gaberdines, etc.

Loose Fibro and Fibro yarns and sliver are now being dyed satisfactorily in some cases by the ordinary method, in others by the use of pigment padding, the Abbot–Cox process, or the improved pigment process using special finely ground dyes.

The use of vat dyes other than indigo, thioindigo, Soledons, or Indigosols is not practicable to any great extent on wool.

The introduction of the various retarding and levelling agents and research into the rate of dyeing of vat dyes has extended the use of package-dyed yarns.

## INTRODUCTION

Package dyeing was introduced for the purpose of preventing damage caused by excessive working in open vessels, particularly so for wool, as far back as 1846, when mordanting used to precede the dyeing. The usual method was continually to stir up the wool with poles to move it about and at the same time to ensure even heating of the liquor. The principle of package dyeing is the same in all systems, namely that of moving the liquor through the material, which is stationary; the only differences lie in the methods of supporting the material to achieve even dyeing.

From the time the first machine was made to the present date many changes in design have been made, the aim having been to get as good a flow of liquor through the material as is possible without distorting the package. If distortion should occur, badly uneven results will be obtained. With cops, cheeses, cones, and beams, even winding and diameter are essential if good work is desired. A tight band either at the end of a cheese or cone or in the middle will result in a light place. Too much tension during winding will allow less liquor to pass through and cause cross-over marks where one thread crosses the other. Too little tension will often result in a blow-out; it is important, therefore, that strict control should be kept on both beaming and winding.

A cone or cheese if not absolutely level will be dyed lighter or darker in the centre than the outside, or at some point between, and if used for weft will make weft bars because the outside is wound on to one pirn and the centre on to another. For warping any slight unevenness can be lost by careful laying in of the ends.

The same fault can apply to beam dyeing, but if the yarn is dyed equally level across the beam, the effect would be apparent only if one compared the first piece woven from it with the last one. With cops there is a different kind of unevenness. Whilst each cop will be alike, the build being conical, the resulting piece will have a skittery appearance and no bars, though some form of patterning may result.

The same remarks apply to viscose cakes as to cheeses unless dyed in the Obermaier type of machine and packed as shown in Fig. 1, where the liquor passes endways through the cake between the layers of the wind.

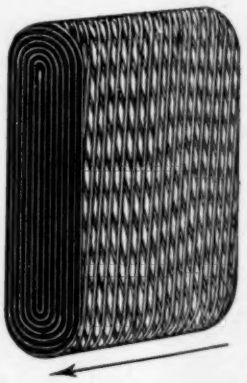

FIG. 1—Flow through Viscose Rayon Cake endways

As the function of the machine is to transfer the dye from the liquor to where it is required, whether it will do so depends greatly on the type of dye being used. Vat dyes strike very quickly, but if it is possible, as it is in a properly wound cotton cheese, for the flow to be more rapid through the package than the rate of strike, little difficulty will be encountered. With viscose in any form of package this is difficult, and other means of bringing about levelness have to be adopted. A step forward in the progress of control in package dyeing was a study of the rate of liquor flow in package dyeing by W. Armfield in 1947 [1]. Further

work along these lines using vat dyes on varying thicknesses and densities of material at different pressures would be welcome.

A machine similar to that described by the author in 1916 [2] built with modern improvements would be capable of helping to solve many of the problems involving time of strike compared with rate of liquor flow encountered in practice.

### THE FIRST VAT DYE— INDIGO

Indigo was the first vat dye to be applied on the package system, more particularly after the discovery of the hydrosulphite vat by Schützenberger and de Lalande in 1871, and was the first to be used for the dyeing of wool in England, the dyer making his own hydrosulphite by killing sodium bisulphite with zinc dust, neutralising with lime, and filtering. The equation according to Hummel in 1885 [3] was—

$$Zn + 3\,NaHSO_3 = NaHSO_4 + Na_2Zn(SO_3)_2 + H_2O$$

Whilst this was quite good, it was not so easy to use as the hydrosulphite powder now known as Hydros, perfected and introduced by the Badische Anilin- und Soda-Fabrik (B.A.S.F.).

on a special machine, where the well reduced vat liquor could be satisfactorily sucked through; this was followed very quickly by a good vacuum extraction until oxidation was completed, before either rinsing, scouring, or re-dipping, in order to produce a deeper shade.

As many as six dips are given, though after the first dip the following ones should only be long enough to obtain even absorption, and should not exceed 90 sec., so as not to bring off any Indigo taken up by the previous dip. The greater the number of dips given to get a final shade the better will be the fastness to rubbing.

It is possible with Indigo to produce some very rich and deep navy blue shades, not surpassed by any other dye. Its washing fastness is not all that could be desired, as it gradually loses depth until after several washes the original navy is almost a sky blue, as many will have noticed from the shade of the collar worn by an older naval seaman compared with that of a new recruit, and from the light blue shade common to engineers' overalls after a few washes.

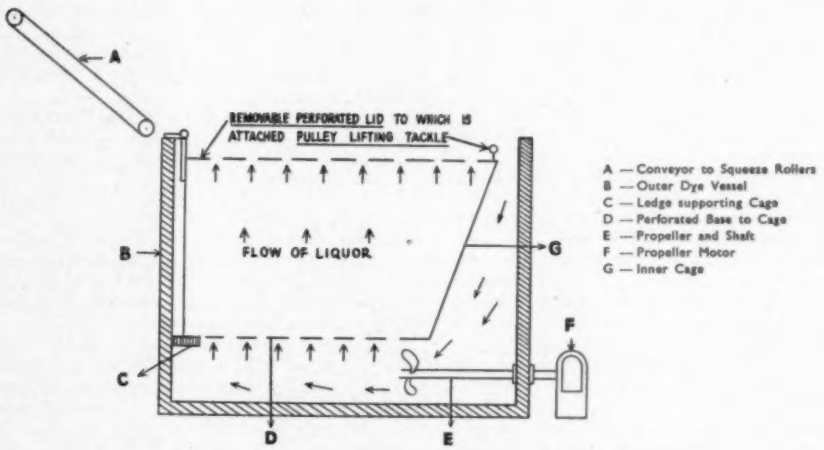


FIG. 2— Diagram showing Principle of Vat Dyeing Machine for Loose Wool

There is little evidence available of any package dyeing with Indigo before 1897, when the B.A.S.F. first manufactured synthetic Indigo in paste and powder form, to be followed later by the making of a reduced form known as Indigo 20% Vat 1, and afterwards by a redder brand, Indigo Vat R 20%, which possessed a better affinity and washing fastness but a slightly lower fastness to light. It was recommended that an addition of glue equivalent to 25% of the amount of Indigo powder strength used should be added to the vat when made up and not to the stock vat, where the concentrated alkali might coagulate it. It was stated that this makes a considerable difference to the amount of Indigo taken up at each dip and gives a better fastness to rubbing [4].

Cops and small softly wound cheeses were dyed

In 1906 there were machines designed for dyeing cops and cheeses, one in particular for continuous dyeing made by Krantz of Aachen, the Graemiger machine [5,6].

In those days cotton yarn dyed with Indigo was considered fast relative to other dyes available. It was later shown by the Deutsche Echtheitskommission (D.E.K.) [6a] to have a light fastness of 3, a washing fastness of 4, and a rubbing fastness of 1. The bleaching fastness left much to be desired, though it would withstand a light chlorine bleach without losing too much colour if the bleach was carefully done. Indigo is still used to a fair extent for sailors' collars, mess jackets, and overalls, though it is dyed in this country not so much by the package system as by the chain warp method. For other goods on the package system it gradually

lost place with the introduction of Indanthren Blue in 1901, Thioindigo in 1906, and Hydron Blue in 1908, owing to their better fastness properties and greater ease of application, being increasingly used again during the 1914–1918 war and later periods when the latter dyes were not always available in this country.

For the dyeing of wool Indigo is still a first-class dye. It took a considerable time before the hydrosulphite vat replaced the older, slower, and less productive fermentation vat. Perhaps this was because the dyeing of Indigo was more a craft than a science and required much experience in order to control a vat, and the old-time dyers were often illiterate in many other ways and suspicious of any new methods. As well as for the dyeing of piece goods, Indigo is still dyed in fair quantities on loose wool and slubbing for the best government, military, police, and naval cloths.

The deepest shades require about three dips. Wool is often dyed by the old system of immersion in a properly set vat, being worked under the liquor for 20 min. It is then forked out, passed through squeeze rollers to remove as much of the excess unexhausted liquor as possible, and allowed to oxidise, after which it is returned to the original vat, which has been fed up with Indigo from a stock vat or with the already reduced Indigo marketed as Vat I 20% in a quantity estimated to be that taken out by the batch of wool. This process is repeated until the desired shade is obtained.

A thorough squeeze is essential in order to produce a good shade or hue with the best possible rubbing fastness. If a wet patch comes through the squeeze rollers, very often white spots will appear around it and the hue will be much duller, an explanation for which I have not been able to find.

In this method much felting of the wool takes place. Afterwards instead of stirring during immersion, a grid was placed on the top of the wool and a propeller used to circulate the liquor (Fig. 2), the wool being afterwards forked out through the rollers. This is really not understood as a full package system.

Indigo is easily applied to wool or loose material by the package system. The best results are obtained when the machine is fitted with an arrangement whereby the container can be used as a hydroextractor, so as to oxidise the dyed wool completely without removing it from the container before giving a further dip. A sketch and description of a combined machine for dyeing and hydroextraction were given by the B.A.S.F.[7]. Very good results are obtained with this machine, where two or more dips can be quickly dyed and oxidised without removing the container.

Other machines are made with a container that lifts out into a separate hydroextractor, where the dyeing is equally good, though they are not so quick or adaptable for returning excess dye liquor back to reserve.

Dyeing in machines not fitted for hydroextraction or with a good vacuum system is not so good, and is done by allowing the excess liquor to drain as much as possible, then first rinsing with cold water containing a little Hydros and ammonia to remove as much unexhausted dye liquor as possible, and finally rinsing with more cold water. This method is not so clean as the former, and the shade is liable to be skittery and flatter.

The exhaustion method is better. In this, after dyeing for 30 min., a solution of ammonium sulphate is dripped into the vat until the latter is neutralised down to pH 7·5, when after a time the vat should be almost completely exhausted; this is followed by either hydroextraction or oxidation in the machine with approx. 2% of 30-vol. hydrogen peroxide at 85°F., souring at 175°F. only if improved fastness to decatising is desired. The strength of the vat depends upon the liquor : goods ratio and the shade required. There appears to be no published work giving figures for the amount of Indigo taken up at varying liquor concentration.

A trial should be made using as long a liquor ratio as the machine will allow, and sufficient Indigo Vat I solution to get the shade in one dip if it is possible, with the least amount of unfixed Indigo. If it is not possible to get a satisfactory shade in one dip, it is better to find the concentration required to give it in either two or three. Experience will quickly enable the dyer to estimate the amount taken up, which is the amount required for replenishing for a further lot or for another dip, or it can be estimated quantitatively by means of a pyridine extraction.

Indigo is still the best and most used vat blue for wool, although it is not so simple in application and particularly in combination with the newer vat dyes described below.

### LATER VAT DYES

In 1906 P. Friedländer discovered Thioindigo; this was closely followed by various derivatives of Indigo— Ciba Blue B and 2B by Engi and other dyes under Ciba, Thioindigo, Helindone, Algole, and Durindone denominations.

From these a very beautiful range of bright shades can be dyed having excellent fastness properties on wool, much brighter than can be dyed by alizarin and chrome dyes. A full list of these and analogous dyes together with methods of application to wool is given by M. R. Fox[8]. In this country these dyes have not been used as widely as they deserve, and a range of dyes as complete as the Helindones is not as yet made in this country.

Loose wool and slubbing can be successfully dyed on all forms of package machines, and are chiefly used for stripes in better-class wool and union shirtings and for pale shades in high-class worsted suitings. Most of them have a high fastness to light and wet finishing processes. Most German army cloths made from wool had to be vat-dyed, one firm having as many as twenty machines designed in about the year 1890 (as shown in Fig. 2) for doing this class of work. This machine was also used for dyeing slubbing in hank form.

The can dyeing machines made by the Longclose Engineering Co. as well as the machines made by Obermaier and others constructed for dyeing slubbing in the ball and hank forms can be used to give successful results.

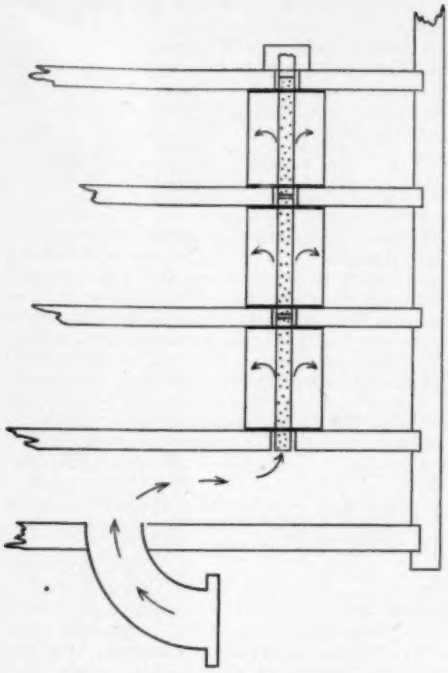

FIG. 3—Mounting for Cheeses with Distance Pieces giving Even Weight on Each Cheese

With the exception of the Indigosol (DH) dyes discovered in 1921 and Soledon (ICI) dyes discovered in 1924, the principle of applying vat dyes to wool has not changed since they were first introduced commercially in 1908, i.e. in the hydrosulphite vat.

For the dyeing of loose wool and slubbing the Indigosols offer no advantage over the thioindigo and brominated indigo dyes. For cops and cheeses, however, they offer the advantage of cleaner and more level dyeings. The Indigosols are not largely used owing to high cost, but their fastness properties put them in a class alone where peroxide bleaching and cross-dyeing have to be done. The main disadvantage is the high acid content of the developing bath, causing excessive damage to many stainless steel machines and metal dyeing tubes. Several machines made of hard wood with porcelain fittings using perforated tubes made of special plastic material are available for dyeing Indigosol, Soledon, Cibantine, etc. dyes, working with a one-way pressure circulation. The softly wound cheeses are built up between hard wood slats, which slightly depress the cheeses to make a good pack, and at the same time prevent the weight of the upper cheese from compressing the under cheese more than the top one by fitting into grooves at the side spaced out to the correct distance (Fig. 3).

These vat dyes, discovered more than forty years ago, are still unsurpassed for brilliance of shade and all-round fastness, and if wool could withstand the boiling wet treatments that are expected of cotton and allied fibres, no doubt the demand for such dyes would be very much greater.

### CELLULOSIC FIBRES

The dyeing of cotton in all forms, either as yarn on cops or cheeses, as sliver, or in the loose state, was practised prior to 1901 to a greater extent on the Continent than in Great Britain; chiefly on cops and cheeses for Indigo and direct dyes, the main use being for checks and fancy goods, often by small vertical firms, who produced a large variety of designs on cheap fabrics.

The vat dyes presented little difficulty in the package dyeing of cotton or similar fibres in the unmercerised state so long as the winding was soft and even, as was the case with a mule- or ring-spun cop, which had to be spun or wound on to either a thin perforated tube or, as was more general, a small porous paper cop the bottom of which extended into the cop about 1 in.[9–11].

Following the introduction of Indanthren Blue in 1901, the B.A.S.F. soon had a fairly good range of Indanthren-type dyes on the market, e.g. Flavanthrene (now Indanthren Yellow G), Indanthren Gold Orange G, Violanthrene (Indanthren Dark Blue BD), quickly succeeded by others, and by 1910 the range included the following Indanthrens—

Red G, R, BN; Claret B; Red Violet RRN
Violet RR, RT, RN, B
Dark Blue BD, BGD
Blue RS, RC, GCD, GC, 3G
Green B (also known as Indanthren Black)
Olive G
Brown B
Maroon R
Grey B
Gold Orange R

most of which could be applied satisfactorily by package dyeing for use in stripes, checks, and fancies, on cottons if suitably packed. The introduction of these dyes revolutionised the dyeing industry and opened a large field for the production of fancy fabrics containing yarn-dyed effects with excellent all-round fastness properties of inestimable value to the consuming public.

In this country the cotton industry is run more by horizontal than by vertical firms, and we have many dyers who specialise in hank dyeing, chain warp dyeing, and piece dyeing, and a few who specialise in cop, cheese, cone, and beam dyeing. Excellent results were obtained by dyeing on the chain or ball warp principle and winding for the weft on the 378-end Holt machine, making warp and weft from the same dyeing, but package dyeing was not looked upon with much enthusiasm in this country until about 1930. A few years before 1912 the American firm of Franklin Process Co. put down in Denton an exhibition plant for dyeing cheeses on a patented special collapsible tube or spiral, on which the yarn to be dyed was wound in order that a solid column of cheeses could be formed. This entailed special winding to give an

evenly wound cheese without being too hard. The diameter of the centre spiral was approx. 1½ in., being wide enough to allow sufficient liquor to feed a column approx. 60 in. long, the outside diameter of the wound package up to 7 in. giving a thickness of yarn through which the liquor passes of not more than 2¾ in. The standard machine was constructed to take up to 1000 lb. of yarn; there was practically no limit to the amount it could be made to hold.

In 1913 John Brandwood of Bury took out a patent [12] for a machine capable of dyeing several specially wound beams, followed in 1923 by a further patent [13] for coupling a number of machines together, thus enabling a larger number of beams to be dyed to one shade. Even in 1905 mention is made of a patent taken out by John Brandwood for a machine to dye 1000 lb. of cops at one dip. One could say that he was one of the most successful pioneers of package dyeing in this country. On the Continent, however, one can go back as far as 1847, to the firm of Johan Wulfing in Lennep. This firm are still using the machine designed over 100 years ago, before the discovery of the first aniline dye, and are dyeing 1000 lb. of wool in top form.

There are pack dyeing machines to-day made by different firms, all somewhat different in design, too numerous to mention. The main principle is to move the dye liquor through a stationary package, firstly to prevent damage to the particular material that is being dyed, latterly and particularly with yarns made from cotton and man-made fibres, to give better production in winding and weaving, etc. Each designer strives to overcome earlier difficulties, namely penetration and channelling, in order to produce satisfactorily level results. This was fairly easy when using direct dyes selected, in the days before the rate of dyeing was investigated, by practical trial and error, a very costly method at times.

In 1915 a series of experiments on the speed of dyeing with direct, sulphur, and Ciba dyes showed that loose cotton could be dyed a level shade through a pack 2 ft. 6 in. thick [2]. Nothing more was done until C. M. Whittaker and his co-workers, Boulton, Morton, Wilcock, etc., set to work to find out the rate of dyeing of direct dyes, a most valuable contribution, which was afterwards investigated by a special committee of the Society [14].

One can safely say that to all intents and purposes the problem of dyeing direct dyes in package machines was solved satisfactorily for dyers of cotton and viscose.

The application of vat dyes either open or by the package system presented a more difficult problem, more so with viscose than with cotton, and particularly so with certain groups of vat dyes of the anthraquinone type known under the names of Indanthren (IG), Caledon (ICI), Cibanone (Ciba), Paradone (LBH), Sandothrene (S), Tinon Chlorine (Gy), etc. These are usually divided into three classes, A, B, and C, called by the German dyemakers IN, IW, and IK respectively. Class A consists of hot strong caustic dyes, Class B warm medium caustic dyes, and Class C cold weak caustic dyes.

When the B.A.S.F. put these dyes on the market before 1909, they recommended the following methods for vatting and dyeing and also the following lists of Indanthren dyes suitable for package dyeing.

*Group A*

| | | | |
|---|---|---|---|
| 100 | gal. | ... | Water |
| 10 | pints | ... | Caustic soda (76° Tw.) |
| 1–1½ | lb. | ... | Hydrosulphite powder |
| 10 | lb. | ... | Indanthren Blue GC |

The same concentration of caustic soda is used for all weights of dye. The hydrosulphite is varied if extra dye is used, with a minimum of 1 lb./100 gal. for small quantities of dye. Vatting is at 120°F. in the complete volume; or in a special vessel when the dyeing of pale shades necessitates the commencement of dyeing at 85°F., running a short time at this temperature, then gradually heating up to 120–140°F., and finishing at this temperature in 45 min. Finally the material is rinsed to remove caustic soda, soured if necessary, and soap-boiled.

| | |
|---|---|
| *Yellow G | Blue GC |
| Yellow R | *Blue GCD |
| *Gold Orange G & R | Blue RS |
| *Orange RT | Blue RC |
| *Copper R | Violet RR extra |
| Scarlet G | Violet B extra |
| Wine G | Violet RT |
| Green B | Dark Blue BO |
| *Blue 3G | Dark Blue BGO |
| *Brown B | Black B (special method) |

*Group B*

| | | | |
|---|---|---|---|
| 100 | gal. | ... | Water |
| 3½ | pints | ... | Caustic soda (76° Tw.) (5 pints for heavy shades) |
| 1–1½ | lb. | ... | Hydrosulphite (more for heavier shades) |
| 10 | lb. | ... | Indanthren Claret B (paste) |
| 3 | lb. | ... | Salt |

The goods are vatted and dyed at 100–120°F. for 30 min. Salt is added slowly, and the dyeing is run for a further 30 min.

| | |
|---|---|
| Red G | Claret B extra |
| Red R | Violet RN |

*Group C*

These dyes are best dyed cold, the procedure being the same as with Group B, with the difference that in the case of Indanthren Red BN less caustic soda is required, about half with double the quantity of salt. With Indanthren Red Violet RRN 1½–5 pints of caustic soda per 100 gal. of liquor is required, varying according to depth of shade. The deepest shades are obtained by dyeing cold.

Yellow GN extra
Red BN extra
Red Violet RRN

At that time the only product mentioned to assist levelling was glue, mainly for the Indanthren Violet R type, a recommendation of 8 oz./100 gal. being made.

* These dyes can be dyed also by process B

These processes have been given in order that they can be compared with methods in use at the present time, particularly those recommended by the Vat Dyes Committee for making their tests [15]. In comparison one finds very little difference. More dyes have since been discovered and placed in one of the three classes. Indigoid dyes have not been given here, as they belong to a definite class and require a different procedure.

With a wound package of cotton yarn on either cheese, cone, or beam, with a dyeing radius of not more than 6 in., sufficiently soft for the contraction which takes place on wetting not to make the package too hard for the liquor to penetrate freely, excellent results were obtained even in the early days. A faulty package or tight threads caused by varying tension or uneven building up of the yarn would result in light places. Owing to the high affinity and high speed of dyeing of some vat dyes, these faults were very difficult to overcome, and often they were not. Glue and special cellulose sulphite waste were the retarding agents then in use. Suitable stripping or levelling agents for vats were not known, and the faults could not be remedied. Owing to these faults, manufacturers were reluctant to have goods dyed by this method whilst they could get satisfaction from warp- and hank-dyed yarns.

The ideal way was to dye in the loose and sliver state and spin afterwards. This had its disadvantages— dyeing in the loose state would make a lot of coloured waste, for which there would not be a large enough use, as anyone who understands the Lancashire cotton yarn trade will know. Spinners specialised in fine or coarse counts, and there were not many mills spinning coloured yarn. Those who did had the cotton dyed in the sliver; this left the waste in the white form, and was adopted more extensively on the Continent by the vertical firms who dye, spin, weave, and finish in one mill.

Whilst the dyeing of yarns in hank form in machines used for loose cotton was advocated, little was done until about 1930; it is now done in large quantities in stainless steel machines with hydroextraction arrangements.

Hydron Blue, discovered in 1908 by L. Haas, was largely used for cop and beam dyeing with success in 1911 owing to the deep rich blue obtained by a simple process in one dip, its fastness being superior to that of Indigo.

During and until well after the 1914–1918 war progress was held up by the lack of vat dyes in this country and the difficulty of importing them. Before the introduction of stainless steel machines, machines for vat dyeing were chiefly constructed of iron in some form or other, having nickel alloy fittings. It was difficult to get absolutely clean results if any part of the yarn had to come into contact with iron, particularly if the body of the machine was made of wrought steel instead of cast irons with a high silica content, which are practically rustless. The introduction of stainless steel for machine construction constituted a marked advance in the application of vat dyes in package machines.

It is well known that the application of vat dyes to viscose rayon yarn in hank form presented not only difficulties in dyeing from a levelling point of view, but created, owing to the more lengthy processing, winding difficulties, which not only made a lot of waste and damaged filaments but added considerably to the cost. Attempts at package dyeing made little progress. In 1922 the author made many attempts to dye Indanthren Blue GCD on rayon in top form through a thickness of 5 in. by using sulphite waste as a retarding agent; the temperature was 60°F., being gradually raised after 30 min. to 130°F. If excess sulphite waste was used, a pale blue only was dyed from 20% of dye paste instead of a good royal shade; this, however, was level. On lowering the quantity of retarding agent better dyeing but uneven results were obtained. With Ciba Blue 2B, as also with Hydron Orange and Helindone Red 3B, satisfactory level shades were obtained. They were not level enough for a yarn-dyed standard, but had to be combed in with wool for cross-dye effects, any unevenness being lost in the mixing. We did not persist further with the dyeing of viscose tops or Fibro until about 1949.

In 1931 G. E. Burgess took out a patent [16] for a machine which is used to-day for dyeing hanks and rayon cakes with vat dyes and Indigosols. It is difficult to estimate what success is obtained with ordinary vat dyes, and it seems probable that a certain amount of repacking would be necessary. With Indigosols, however, I have seen a battery of six containers packed with 12–14-oz. rayon cakes, 200 lb. in a container, making 1200 lb. in one dyeing, give a very satisfactory light peach shade.

About 1937 Messrs. Courtaulds Ltd. and the Longclose Engineering Co. produced a closed machine for dyeing cakes on a special built-up form of cake-holder. Some success was obtained with vat dyes that would withstand high temperatures. Whilst much research and experimental work was undertaken with both pigment padding and direct application from the leuco vat, they never claimed it a success. There is no doubt that the work published by Boulton and Morton in 1939 ("Strike Index Classification of Vat Dyes") [17] has been of great assistance to all users of vat dyes.

At about that time rayon staple was coming into prominence either loose or in the form of yarn or sliver, and the demand for vat dyes naturally followed. Gold, brown, and green shades were dyed in bulk in Obermaier or similar machines and on a specially wound cake on Longclose or the Courtaulds horizontal-arm machine [18] either by the pigment padding method or from the reduced vat. No mention is made of any success with the anthraquinone vat blue dyes; these were a difficulty to be overcome later.

A satisfactory method of applying vat blues had not been worked out by 1945, when the Abbot–Cox process for the application of vat dyes in a dispersed form was patented [19]. The novelty of the discovery was that salt could be used for exhausting dispersed pigment from the pigmentation liquors on to the fibre, by acting as an aggregating agent, gradually enlarging the particle aggregates until

they filtered out inside the package. The amount of salt used varied with the dye used, some dyes requiring no salt. It was essential that the dye liquor should be thoroughly exhausted before reduction, since any unexhausted pigment would on reduction dye on to the outside or inside of the package and produce unevenness. The inventors did not claim that all dyes could be distributed evenly throughout a cake of viscose, heavy shades being more difficult to attain than light ones. This invention was certainly a marked advance, particularly for loose Fibro and sliver dyeing, and many pounds of vat blues and greens have been dyed by this method that otherwise would not have been dyed. On Fibro yarn and warps good results were obtained with difficulty and involved repacking two or three times during pigmentation.

The vat acid process was first used by the late Dr. Storey for dyeing certain vat dyes on cellulose acetate fibres, and was later advocated by the I.G. in Germany as a means of dyeing tightly packed viscose rayon fibres or yarn. This method was investigated by I.C.I., who state that in package dyeing the most critical part of this process is the slow addition of the alkaline reducing agents [20]. If this addition is made correctly, results are obtained which are decidedly superior to those obtained by the normal method as regards penetration and levelness. This superiority is most marked in pale shades, particularly with the rapidly dyeing Group C dyes, but in their experience equally good results are obtained with less trouble by the judicious use of retarding agents such as Dispersol VL. In my opinion this statement applies to cotton or similar yarns but not to viscose packages or cakes, as finally I.C.I. state that no really satisfactory way has yet been devised for dyeing viscose rayon cakes by this process.

H. H. Hampson [21] discusses the use of very finely divided pigments obtained by a special regrinding of normal vat dyes which sometimes takes up to seven days. He states that this represents a great advance over the leuco dyeing method or the original Abbot–Cox process. It has enabled the production for the first time of a satisfactory range of shades vat-dyed on rayon cakes to a commercially acceptable standard of levelness and processing condition of dyed yarns. The process appears not to be difficult or lengthy, and can be applied to viscose rayon in all forms, either loose, sliver, or yarn.

Indigosols (DH), Soledons (ICI), Cibantines (Ciba), etc. possess little if any advantage over ordinary vat dyes on ordinary cotton yarns if the latter are correctly wound in packages of the right size with a dyeing radius of not more than 6 in. These dyes, which are very soluble and generally of poor substantivity, can be applied successfully even in light shades to viscose and mercerised yarns. They vary widely in their rate of exhaustion, salt sensitivity, and temperature of maximum substantivity (or affinity). Full details of their application are given by Christ [22] and by Whittaker and Wilcock [23], the latter giving a table of salt sensitivity, rate of dyeing, temperature, and percentage of salt for maximum affinity. These dyes are of advantage for light shades only, or where difficulties of penetration and levelling cannot be overcome by ordinary vat dyeing methods. They present oxidation difficulties which are fully dealt with in the above references. Owing to the high acid content of the developing baths, sometimes as high as 10 c.c./litre, only machines that will stand this concentration of acid should be used, or excessive damage to the machine will result.

In this general review of progress made in the application of vat and Indigosol dyes in package machines, little if anything has been said about vat retarding or levelling assistants such as Peregal O (IG) introduced about 1930, maybe a little earlier, followed later by other products such as Albatex PO (Ciba), Lissolamines (ICI), polyvinyl alcohol, Dispersol VL (ICI), etc., all of which have made a definite contribution to the successful dyeing of vat dyes. A valuable paper on the restraining action of Dispersol VL by Speke [24] is worth the attention of all users of vat dyes, also one on the "Redox Potential of Vat Dyes" given by R. H. Peters at Lille in May 1951 [25].

Since writing the above, I understand that the B.A.S.F. have put on the market under the name of Colloisol a finely divided vat dye which they claim to have a particle size 0·01 time that of the normal powder fine brands. One German machine maker informed me that they can be applied to viscose cakes like an ordinary direct dye, and then reduced and finished *in situ*.

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## Discussion

Mr. H. Hampson: The dyeing of the Colloisols does not appear to resemble that of ordinary direct dyes, but appears to involve the same principle as claimed for the Abbot–Cox pigmentation–reduction process, viz. aggregation by the salt of the dye particles, so that they filter out in the viscose rayon cakes. The Colloisols, being of very fine particle size, much smaller than normal dye pigments, require a considerably larger quantity of salt to bring them to the size at which they start to filter out. The same applies also to the reground pigments used at Droylsden[21], although these are not so fine as the Colloisols.

Mr. Smith: I saw at Ludwigshafen a cake dyed with Indanthren Blue RS Colloisol. The dye just dissolved in cold water of zero hardness was passed through two thicknesses of filter paper and left no residue. Dyeing was commenced at 130°F. and kept at this temperature until complete exhaustion was obtained by adding 5 g. of desiccated Glauber's salt per litre every 10 min.— in all 85 g./litre and a dyeing time of 170 min. On examination the cake appeared satisfactorily level and as if it had been dyed with a direct dye. It was afterwards vatted in a fresh bath with caustic soda, Hydros, and 1 c.c. Albigen A per litre, starting at 130°, raising to 160°F. in 30 min., and running a further 30 min. I have since received this cake after final soaping, and it is excellent.

There is probably some effect other than just filtration, in view of the evenness with which the particles are deposited. The remark applies also to the Abbot–Cox process and the improved method of Mr. Hampson.

Mr. Hampson: Our experience at Droylsden has been that, using the reground vat dyes, no repacking of Fibro yarns and warps is necessary during pigmentation.

Mr. J. Boulton: It may be that, because of electrical surface forces, there is not a definite correlation between filtrability and particle size. But Hampson's work[21] *has* shown the correlation between cake levelness and particle size to be complete; i.e. fine particles of $> 2$–$3\ \mu$. give level results, while coarse ones do not.

Mr. S. Emmott: With a tightly wound package such as a cotton beam, how do you achieve satisfactory oxidation and hence level dyeing?

Mr. Smith: All the packages on exhibition were rinsed and oxidised by the flooding method, in which at all times the package is under liquor, so that no part of the package comes in contact with air until all surplus or unexhausted dye liquor is removed. No vacuum or hydro-extraction was used.

Mr. T. Flanagan: In the vat dyeing of viscose rayon cakes, more and more emphasis seems to be laid on the value of an evenly pigmented cake, and it is stated that the dye liquor must be thoroughly exhausted before reduction. Hampson has reground commercial dye pastes to achieve this. Nevertheless, even when a dye liquor is 100% exhausted, a considerable amount of dye is returned to the bath as soon as the caustic soda and hydrosulphite are introduced. This can be as much as 60% of the dye originally padded into the cake, a notable exception being Caledon Blue RC. When dye is returned to the bath in this manner, level pigmentation assumes less significance. We appear to be overemphasising the importance of pigment padding, and we should turn our investigations in other directions to arrive at a satisfactory answer to the problem of the vat dyeing of viscose rayon cakes.

Mr. Smith: Some vat dyes can be dyed without a pigmentation method. Many dye so rapidly that no satisfactory method of applying them through a viscose cake or thick package of other cellulosic fibres or yarns by the leuco vat method has yet been found.

It is obvious that a dye of which 60% will bleed off from the inside of a cake does not need to be applied by the pigmentation method, unless levelness can be attained quicker that way.

Mr. C. P. Atkinson: As a matter of historical interest, Messrs. Courtaulds Ltd. (Coventry) bought part of the plant referred to in the paper (Franklin Process Co., Denton) in 1931. This was at first used for dyeing continuous-filament viscose rayon and Fibro in cheese form using principally direct cotton dyes, although experiments were made with vat dyes and Soledons. The collapsible spring containers were at first used, and later perforated stainless steel tubes, both with successful results, more particularly on Fibro. The large machine was altered in 1933–1934 and lined with a rubber composition; the spindle plate was fitted with tubes suitably spaced to take standard perforated cake holders, and the machine was then used successfully for cake dyeing (416 viscose rayon cakes on 26 spindles). This machine was possibly the first bulk cake-dyeing machine. As a result of the success of this machine, a new all-stainless-steel machine— on a pressure dyeing reverse-flow principle— suitable for dyeing viscose rayon cakes, previously dried, was ordered from Messrs. Franklin Rayon Inc. (Providence R.I.), and put into operation in Coventry in 1936.

Dr. C. M. Whittaker: If the pirns are woven in the strict rotation of their winding from a package, and the pirns from the next package woven in strict rotation, care must be taken that, if the last pirn was from the inside of a package, then the first pirn from the new package must be the pirn made from the inside of the package. Mr. Adam Glover of Courtaulds Ltd. first applied this method with viscose rayon cakes to eliminate bars.

Mr. Smith: In the days when viscose in yarn form dyed differently one hank from another, a fault which the good spinners have almost overcome to-day, all wound pirns had to be graded out and used in sequence to obviate bars. All dyed packages are liable to a slight difference from outside to inside; this can be caused in drying as well as in dyeing. I am glad to know that some weavers take the precautions mentioned by Dr. Whittaker. It must save many faulty pieces.

# The Application of Direct Dyes to Viscose Rayon Yarn and Staple

J. BOULTON

Dyeing theory has been very largely worked out on the basis of regenerated cellulose substrate and direct dye. Improvements in the dyeing of viscose rayon have followed closely developments in fundamental understanding of the dyeing process.

This paper gives the history of the dyeing process with direct dyes, a comprehensive survey of the theory, and a statement of the best modern practice with respect to yarn and fibre dyeing. The objects have been to make dyeing theory intelligible to those responsible for dyehouse work and further to relate it to recommended dyeing practices.

A section is devoted to future trends in dyeing practice and to outstanding requirements for new dyes.

## Preface

This paper is an attempt to survey the application of direct dyes to viscose rayon fibres in theory and in practice. It is hoped that it will be intelligible to those who are dyers but not scientists, and no less to those who are scientists and not dyers. To those who have worked in the field, viewing its problems from both sides, I ask a special indulgence if some things are made to appear too simple. Many practical dyers, perfectly at home facing the immense complexities of their art, have told me that dyeing theory is too difficult. For myself I have found the postulation of theoretical ideas relatively simple in comparison with the job of actually dyeing something. What we have to aim at is the achieving of common ground. As a prelude to attempting this, I would like to air two private beliefs— (i) Any theory that cannot be stated in language intelligible to a literate person, at least to an extent where that person has learnt something worth knowing, is a bad theory. (ii) The scientist who takes upon himself the elucidation of industrial processes must know the technology of those processes; in industry, as distinct from purely research institutes, there is no longer any clear distinction between the scientist doing a useful job and the good technologist.

## I— Historical Survey

Viscose rayon has played so large a part in the development of direct dyeing theory and technique that both aspects must be treated side by side in any attempt to review progress in the application of direct dyes to that fibre. In the early years of this century, when continuous-filament viscose rayon was established as a textile fibre, it was assumed, correctly, that its dyeing properties must perforce resemble those of native cellulose. Cotton dyeing methods were attempted *in toto*, and from the start direct cotton dyes took pride of place in the coloration of the new fibre. Cotton dyeing tradition had established this class of dyes as the simplest in application. The early viscose rayons were physically weak and of variable characteristics, and thus, economics and end-uses apart, it was natural that a chemically inactive one-bath dyeing process should receive first attention to the exclusion of two-bath mordanting and coupling methods, or strongly alkaline vat and sulphur dyeing methods. This picture changed in time, with the improvement of the fibre and its accepted use in the manufacture of all types of textiles, and to-day a great proportion is dyed with vat, azoic, and sulphur dyes. In fact, viscose rayon is dyed, according to the degree of fastness required, with all classes of cellulose-substantive dyes. But a much greater proportion of direct dyes than of any other single class is, as with cotton, still used.

The first published investigations into the behaviour of direct dyes on viscose yarn were those of Wilson and Imison in 1920; they found that some direct dyes tended to produce level results and some tended to accentuate unlevelness, and classified dyes accordingly. C. M. Whittaker, establishing a dyehouse for the commercially successful dyeing of viscose rayon, immediately enquired further into this classification. His first refinement was to show that the level-dyeing members of the direct class exhibited a small capillary rise up a thread of viscose suspended in a dye solution, while the unlevel-dyeing showed a relatively greater rise. This was a clear indication of the wide differences in substantivity within the direct dye class. He showed that level results could be expected only from those dyes which tended to migrate from a dyed to an undyed skein. This was a clue to the existence of a diffusion process within the fibre. He demonstrated that if, on dyeing for a fixed time, maximum affinity was established at a low temperature, the dye under test would be level dyeing; if at a high temperature, it would tend the other way. This observation connected dyeing temperature with dyeing rate, a vital relation, later to be interpreted in terms of diffusion kinetics. Above all he established that no two dyes behave alike, and further that, with the most perfect fibre, any mixing of dyes that included members from opposite ends of any of his scales would give trouble to the dyer.

These sound counsels, the results of prescient empiricism, constituted the rayon dyeing "know-how" of the early 1930s. In that year two new laboratories undertook to enquire into the physico-chemical nature of dye absorption by cellulose. Both chose direct dyes for their simplicity of

application and both chose viscose as the substrate, the latter because by then it was sufficiently uniform in properties to provide a standard working material, and it could be obtained in predetermined geometrical shape (as rod or sheet) and of varied filament size. The author benefited from working in both schools, in the Cellulose Chemistry Laboratory of the Manchester College of Technology with S. M. Neale and in the Textile Research Laboratories of Courtaulds Ltd. with T. H. Morton. Using the methods of physical chemistry, these two laboratories established that dyeing was essentially a diffusion process which approached an equilibrium dependent upon dyebath conditions, and they elucidated the influence of dye concentration, electrolyte concentration, type of electrolyte, liquor length, and dyeing temperature on the amount of dye absorbed and the rate of its absorption. Other British laboratories later began to contribute, and notable work of a high order came from T. Vickerstaff and collaborators at Imperial Chemical Industries Ltd. Dyestuffs Division and H. A. Standing and collaborators at the British Cotton Industry Research Association. Papers from these two schools have greatly advanced our understanding of two much abused dyers' terms—"affinity" and "substantivity".

The dyemakers generally took notice of these developments, and in recent years have applied the results to a sorting of their direct dyes according to the properties revealed. A notable example has been the Geigy Co.'s exhaustive technical data provided for all their direct dyes. Other important contributors have been J. M. Preston, notably on optical aspects, F. Fothergill, and G. L. Royer; more recently J. Crank has developed much-needed mathematical methods for treatment of dyeing kinetics data.

In 1944, acting on a suggestion of our President, Mr. F. Scholefield, the Society set up a Committee on the Dyeing Properties of Direct Dyes, to codify the findings of these various research schools up to that time in terms which the dyer could apply in a practical sense. Its Reports were published in 1946 and 1948, and provided the soundest counsel in the selection of direct dyes available up to that time.

In short, research into the nature of direct dyeing has, in twenty years, taken us from a handful of empirical tests to a branch of mathematical science; at the same time it has provided the practical dyer with a deeper working insight into the problems of his art. To no other type of dye on any other fibre has anything approaching this degree of study been applied; at the same time it is clear that the study of direct dyes, largely with viscose rayon as substrate, has produced an acceptable theory of dyeing which in essentials

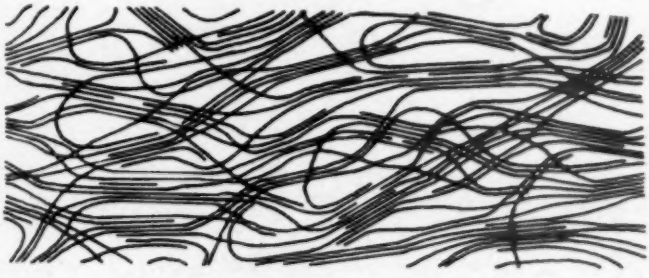
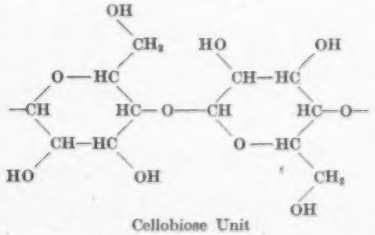


FIG. 1

applies also to other dyes and other fibres. Let us now briefly state this theory in terms of the direct dyeing of viscose rayon, and then attempt to indicate how modern dyeing practice makes use of it in the dyeing of yarns and staple fibres.

## II—The Theory of Viscose Rayon Dyeing

Viscose rayon, like all other textile fibres, is made up of polymeric chains, the links of the chain being in this case cellobiose units—



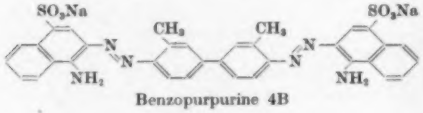

Cellobiose Unit

The chains are packed together to form filaments (Fig. 1). This molecular packing is not uniform throughout the fibre, but, as a consequence of tension applied during the regeneration of cellulose chain molecules from viscose solution to form a

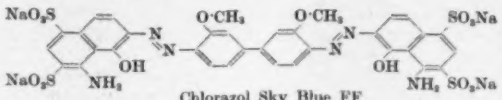
thread, the chains lie roughly parallel to the fibre axis. In some parts, chain molecules are so closely packed that they form crystals, and at others they are twisted together amorphously.

When a filament is wetted, water is strongly absorbed, osmotic pressure pushing aside the disordered chains in the amorphous parts to accommodate an amount of water approximately equal in weight to the weight of wetted fibre; the crystallites remain unchanged. This pushing aside creates pores in the structure, and it is via these pores that dye molecules make their way during the dyeing process. The process by which any solute distributes itself in a solvent is that of diffusion, and dyes enter and traverse the water-filled channels by that essentially simple natural process.

Direct dyes are invariably derived from azo compounds which have substituent sulpho groups to render them water-soluble, and the dyes themselves are the sodium salts of the resulting sulphonic acids, e.g.—



Benzopurpurine 4B



Chlorazol Sky Blue FF

These dyes are made by coupling benzenoid structures together via diazo reactions, the starting points being compounds such as benzidine in which the coupling groups are at opposite ends of the molecule. Consequently the resulting dyes all have "long" structures. Generally speaking, if a dye does not have this linear or rod-like structure, it is not substantive to cellulose. In solution, direct dyes like all other salts are ionised—

$$DSO_3Na \rightleftharpoons DSO_3^- + Na^+$$

But they are ionised in a special way. The molecules tend to aggregate together into tiny dispersed particles; the sodium ions have greater freedom of movement than the large coloured dye ions, and yet cannot escape completely from the attraction of the latter, so that a dye molecular aggregate exists as a bundle of dye anions surrounded by a layer of sodium cations ⊕ and, if common salt is present, chloride anions ⊖ (Fig. 2).

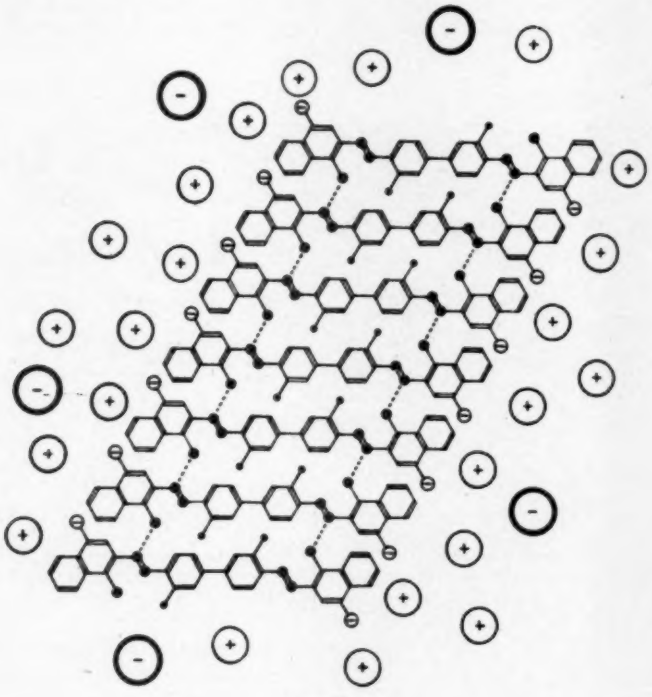


Fig. 2

A solution of a direct dye consists of a dispersion of such bundles which may vary widely in dimensions, from simple dye ions to very large aggregates.

This behaviour is implicit in the description of direct dyes as *colloidal electrolytes*; in solution they exhibit such colloidal properties as gelling, salting out, thixotropy, and streaming double refraction, and at the same time behave like electrolytes in the conduction of an electric current and the development of osmotic forces. Like other similar colloids, dyes in solution are affected by changes in temperature and the addition of other electrolytes. The higher the temperature of the solution the more nearly molecularly dispersed the dye. The addition of e.g. common salt increases the degree of aggregation. (Many dyes may be completely precipitated from weak solution as semi-solid gels by addition of sufficient salt.)

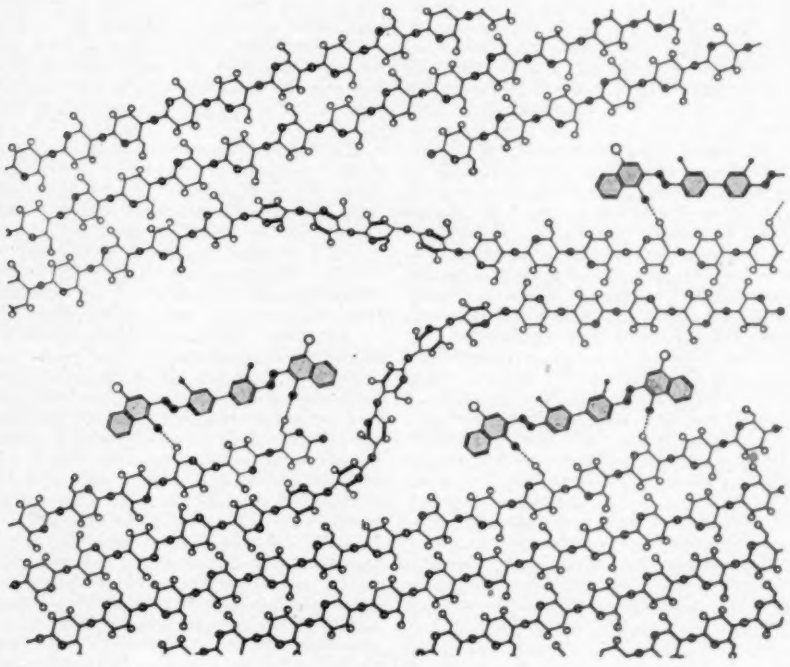


FIG. 3

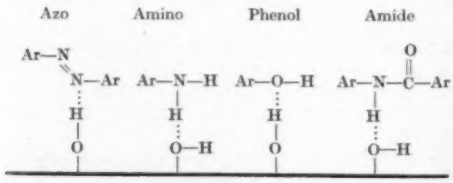
The viscose rayon filament carries a negative electrical charge on its surface. Dye anions are by definition also negatively charged. Because of this, if we take an absolutely pure dye in electrolyte-free water its substantivity towards a pure cellulosic substrate is either nil (Sky Blue FF) or very small (Benzopurpurine 4B), since the like charges repel each other. In order that dyeing can take place, dye ions must make contact with fibre as a prelude to penetrating the surface via the water channels. A pure dye cannot do this; but if salt is present in the dye solution, this preliminary absorption takes place. The reason for this is that the first effect of electrolytes is to suppress the repulsive force between dye and fibre surface, if not completely, to a point where Brownian movement of dye aggregates can overcome the weakened electrical barrier. Thereafter, the addition of further quantities of salt has the effect of lowering the solubility of dye and shifting the equilibrium absorption in favour of the absorbing fibre.

Salt additions are essential in direct dyeing, and the above explains why. But we have seen that salt affects the state of solution of the dye as well as its attraction for fibre. This is of immense practical significance. The first stage in dyeing is the contact between dye aggregates and fibre surface. These aggregates, if they are small enough to enter the pores, diffuse into the fibre, and the dye solution becomes impoverished of single molecules and smaller aggregates. It is in the nature of a polydisperse solution to maintain an equilibrium between large and small aggregates, and as the smaller ones disappear the large ones break down, so that a dynamic equilibrium exists. Now salt tends to aggregate dye molecules; if too much is present, the dye micelles adsorbed on, or situated near, the fibre surface grow rapidly, and we have the accumulation of relatively insoluble dye on the most accessible parts of the fibre

surface. This, in dyeing a mass of fibres in any form, is what the dyer knows as a bad strike, the prelude to a non-uniform dyeing.

Once inside the pores, dye molecules diffuse throughout the amorphous fibre matrix; but if that were all, there would be no exhaustion of the bath other than by that amount of dye soluble in the water which the swollen fibre has imbibed. What, in fact, happens is that diffusing molecules become attached to the internal molecular structure, i.e. they exhibit substantivity, which means that there must be some attractive force operating similar to that which causes dye molecules to associate tenaciously with each other in water solution. This kind of cohesive force operates in a great many chemical systems and substances, and is envisaged as made up of weak forces of attraction to which modern research has given the name *hydrogen bonds*. We have already, implicitly, anticipated the existence of some such forces in our models of a fibre and a dye molecular aggregate. It is the attraction exerted for hydrogen atoms of one chain by neighbouring oxygen atoms of another that holds the cellulosic chains together in fibre formation. This combining energy, which both operates between dye molecules to form dye aggregates and between cellulosic chain molecules to impart tensile strength to fibres, is clearly available to operate between dye molecule and fibre chain molecule when they are brought into contact. The energy of hydrogen bonding can be measured, and that associated with a single hydrogen bond is very small. The lateral force which holds amorphous cellulose chain molecules together is manifestly *not* small, and derives from the fact that each chain molecule has the capacity to operate such a bond at scores of places along its length, operating like a zip-fastener, at every point where there is a properly positioned hydroxyl group. A direct dye is substantive accordingly, as *it also* has several hydrogen bonding groups positioned *along its length*, and that is why the rod-like shape associated with direct dyes is important.

Examples of chemical groupings capable of hydrogen bonding with hydroxyl groups of cellulose are as follows—




Azo, amino, amide, and phenolic groups are common substituents of direct dyes, and some indeed *must* be present, or groups of similar activity, in any dye which is substantive.

The complex formation between viscose rayon and direct dye may be visualised as in Fig. 3, in which the dye molecules are shaded, while the cellulose chains are unshaded.

This picture is confirmed by the optical behaviour of dyed fibres. Thus they exhibit dichroism, i.e. they absorb light polarised in one direction and not in another, which means that each dye molecule must be oriented in the same direction with respect to the fibre axis. This dichroism is not complete, because the orientation of the fibres is not perfect. But the more perfectly oriented the fibre, the more dichroic when dyed, i.e. the greater the degree to which dye molecules are lying in the same direction.

We see the dye absorption now as consisting of four processes—the opening up of the fibre structure by water swelling, the adsorption of dye aggregates on the fibre surface, the diffusion of dye molecules or small aggregates into the capillaries of the swollen fibre, and the fixation of dye molecules by formation of a bonded complex with cellulose chain molecules in the inter-structure of the fibre.

The technical importance of swelling to a true dyeing operation is universal with all fibres and dyes, incidentally. With e.g. hydrophobic synthetic fibres, some means of swelling is a natural essential in the dyeing process.

Under constant conditions of temperature and dyebath composition, the swollen fibre absorbs dye gradually, and in time a state of equilibrium is reached between dye solution and fibre such that the partition of dye between the bath and the dyed fibre remains constant.

The dyer does not always dye to equilibrium, firstly because it may take too long, secondly because he may not have constant conditions; he has a definite shade to match, which is the decisive factor in the dyer's work, he may be making periodic additions of dye or salt, and he may increase or decrease the dyeing temperature or liquor length. We must, therefore, enquire further into the influence of these practical variables of the dyer on the fundamental processes involved.

The swelling process is not affected by dyebath conditions. A viscose yarn or fibre (unless it is waterproofed by size or hydrophobic oils, which should not be the case when it is prepared for dyeing) wets out immediately in water, and the degree to which it swells is not sensibly affected by the presence of any electrolytes or other solutes, nor by temperature.

Dyebath variables influence mainly the rate of dye absorption and the amount of dye absorbed. In both these respects regenerated celluloses are different from cotton cellulose. Viscose rayon has a greater affinity for direct dyes than has cotton; under given dyeing conditions it absorbs dye more rapidly and absorbs more of it, and these facts have led to the more important points of departure from cotton dyeing practice.

### 1. INFLUENCE OF VARIABLES IN PRACTICAL DYEING

If Fig. 4 represents the theoretical course of a direct dyeing, we can best demonstrate the various influences at play in the course of practical dyeing by a series of similarly simple diagrams. In practice the dyer is able to alter all the variables we shall consider; but all he is able to *observe* is

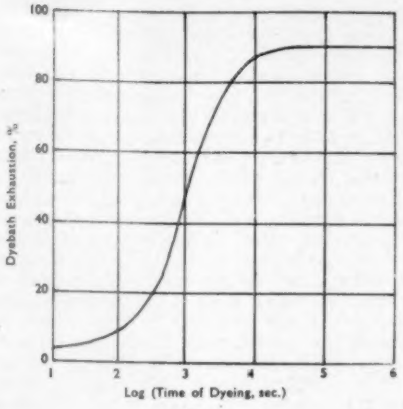



FIG. 4

the rate at which his dyebath is becoming exhausted and how near or how far he is from the required depth and uniformity of shade. Therefore, at the risk of a little oversimplification, we will observe the influence of his practical variables in terms simply of dyebath exhaustion and time.

### (a) *Temperature*

The effect of increasing temperature is to increase the rate of diffusion of dyes in the fibre. Levelling is the process in which dye diffuses from overdyed to underdyed places. All dyeings begin by being non-uniform, since dye is first taken up by adsorption on to surfaces and must afterwards penetrate inside. Many single threads exposed equally to this initial adsorption (strike) may be uniformly coloured to the eye, but they are not penetrated until the diffusing process has operated. A woven fabric, and certainly a packaged mass of yarn, will be initially non-uniform simply because in any dyeing machine it is impossible to expose every filament surface simultaneously and equally

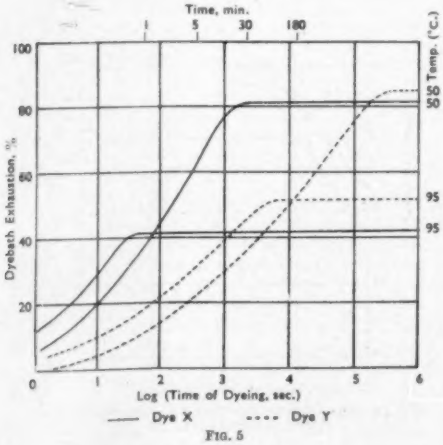



FIG. 5

to the unexhausted dyebath. Therefore, the higher the temperature of dyeing the more rapidly will a level result be achieved.

The further effect of increasing temperature is to lower the amount of dye absorbed at equilibrium. This may seem puzzling to the dyer, because he is aware by practical experience that—

(i) Different dyes "draw", i.e. show maximum (apparent) affinity, at *different* temperatures.

(ii) Raising the temperature of his dyebath may with some dyes enable him to adjust his shade in a downward (thinner) direction and with others in an upward (thicker) direction.

To explain these observed facts we have first to appreciate that the rates at which direct dyes diffuse vary over a colossal range. For example, under dyeing conditions arranged to give the same final exhaustion for both dyes, it takes Durazol Orange 2 GS 2500 times as long to be exhausted as Chlorazol Fast Orange GS.

Now let us consider two such dyes, X being a rapidly diffusing and Y a slowly diffusing type. (The time scale in Fig. 5 is compressed logarithmically so as to show everything on one diagram realistically.) If we apply dye X for 30 min. at 95°c., it will have long since reached its maximum exhaustion, and longer dyeing has no effect. If we do the same at 50°c., we again reach an equilibrium; but it is a new equilibrium, the dyeing being much darker. The dyer has, therefore, called X a "cold drawing" dye. What he really implies is that X diffuses so rapidly that, even when slowed down by lower temperatures, it has still reached its final equilibrium in a short time (30 min.). If we dye Y for 30 min., we have a fractional exhaustion at 95°c., but because dyeing is proceeding *faster* at that temperature than at the lower, the half-hour dyeing at 95°c. is darker than that at 50°c., and Y will be called a "hot drawing" dye. Thus, though to the dyer X and Y may seem to behave in diametrically opposite senses with regard to temperature changes, they are in fact behaving in a similar manner, as theory indicates, except that one dye diffuses rapidly and one slowly. This is also the explanation of the "temperature range" test of C. M. Whittaker, which was in effect a means of differentiating between rapidly diffusing (level dyeing) and slowly diffusing (unlevel dyeing) dyes, for the reasons given.

### (b) *Salt and Dye Concentrations*

The effect of adding salt to the dyebath is observed in practice as an increase in the degree of dyebath exhaustion— we get a heavier shade and the bath exhausts more rapidly. We use salt to exhaust the dyebath wherever we can because salt is cheaper than dye.

If we were to add increasing amounts of salt to a series of identical dyeings and take the dyebath resulting from each addition to equilibrium, we would find that the final amount of dye absorbed by each dyeing depends on the salt concentration (Fig. 6).

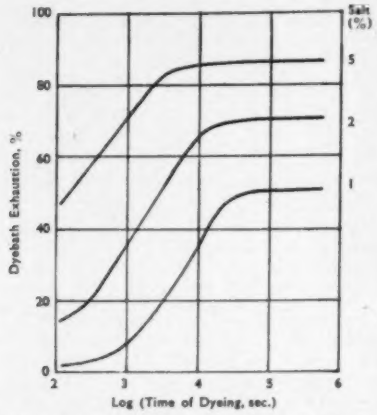



FIG. 6—0·05% Pure Chlorazol Sky Blue FF on 150/27 Viscose Rayon in 25 vol. at 90°C.

The fact that increasing the concentration of salt for a given dye concentration increases the proportion of dye finally taken up by the fibre from the bath may be stated in another way, viz.—decreasing the concentration of dye for a given salt concentration increases the amount of dye taken up expressed as a proportion of the dye present (Fig. 7). In other words, dye concentration and salt concentration are completely interdependent. Research on dyeing equilibrium has demonstrated that, if we express substantivity as the proportion of available dye to be absorbed at equilibrium, then it depends directly on the *ratio* of the salt concentration to the dye concentration. The higher the salt : dye ratio the greater the substantivity of a given dye, i.e. the greater the affinity of the dye for the fibre—

$$S = \frac{\text{Dye absorbed}}{\text{Total dye present}} \propto \frac{\text{Concn. of salt}}{\text{Concn. of dye}}$$

or

$$\text{Exhaustion (\%)} = f\left(\frac{\text{Concn. of salt}}{\text{Concn. of dye}}\right)$$

The degree to which salt : dye ratio determines substantivity varies very widely between dyes, some dyes requiring many times their own weight of salt to exhaust to an economically high degree; while others, if the dye concentration be low enough, are capable of exhaustion in the absence of added salt, the effect being produced by adventitious electrolytes generally found in industrial waters and dye powders.

The extent to which salt additions increase the speed of dye absorption also varies from dye to dye. Now the effect of salt in increasing dyeing speed is not at all similar to the effect of temperature, which acts in the same direction as we have seen. Rise in temperature causes an increase in the rate at which dye diffuses into fibre; salt additions do *not* have this effect to any useful degree. Determination of relative diffusion constants has shown that, whereas diffusion rates may vary between individual dyes by some thousandfold, and for a given dye at different temperatures by some hundredfold, the variation of electrolyte concentration over the practical range varies the rate of diffusion of a given dye only two- or three-fold, which is negligible for the practical dyer. What we have done, by adding salt, is merely to increase the amount of dye which becomes concentrated on and around the surface of the fibre in a given time. That is to say, that the indiscreet addition of salt to a dyebath increases the probability of a bad strike. A bad strike simply means that the dyer has lost control of the exhaustion of his dyebath, and the dye is rapidly deposited on the most accessible parts of the fibre mass, only distributing itself thereafter by the processes of diffusion between the water layers which separate packed filaments and within the fibres themselves. Thus, the addition of salt never assists levelling; it tends always the other way. A dye which tends towards unevenness as a result of minimum salt addition we call *salt-sensitive*. A dye which can be exhausted progressively by salt addition, and which still levels at a rate determined by its diffusion characteristics, we call *salt-controllable*.

### (c) *Liquor Ratio and Agitation*

The effect of decreasing the liquor : goods ratio is to concentrate the dyebath (dye and salt) and consequently to increase the rate at which the dye is absorbed, and also the amount absorbed if equilibrium be reached; i.e. the dyebath exhaustion for a given time is increased. This means that, for a given depth of a given dye (combination), the degree of care which the dyer exercises must be greater the lower the volume in which he is working, since he has less control over exhaustion.

Any increase in movement of dye liquor with respect to fibre increases the probability of dye particles coming into contact with fibre surface, so that agitation must increase rate of exhaustion. Now, a dense mass of yarn in a moving dye liquor comes into contact with the dye at the surface of

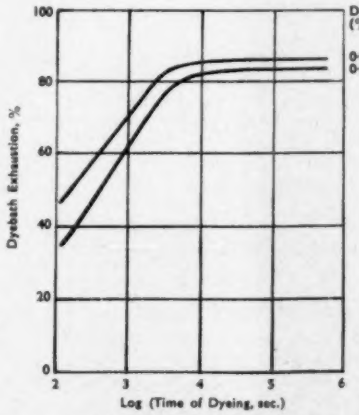



FIG. 7—Pure Chlorazol Sky Blue FF + 5% Salt on 150/27 Viscose Rayon in 25 vol. at 90°C.

the mass, and the interior gradually wets out with dye solution until the mass has absorbed its water of imbibition. Thereafter, the supply of dye particles to the interior depends in part upon the rate at which fresh dye liquor can penetrate. If, because of density of package, that penetration is very slow, agitation of the dye liquor outside will merely help dye to adsorb on to the package surface. If, however, the package can be readily penetrated by the moving dye liquor, increased agitation assists in the initial distribution of dye at the adsorption stage, so that a more uniform strike, throughout the mass, results.

### 2. TECHNICAL CLASSIFICATION OF DIRECT DYES

As the above picture has gradually emerged, workers have attempted to interpret it in practice by various systems of dye classification. Capillary rise (suction) test, temperature range test, salt range test, time–salt test, time of half-dyeing, diffusion constant, dip test have all been expounded in the *Journal* and have helped to serve the dual purpose—(i) of characterising dyes according to levelling properties, and therefore readiness of application; (ii) of indicating which dyes may and which may not be used together in the dyeing of compound shades.

In its reports, the Society's Direct Cotton Dyes Committee put forward a system for the classification and selection of dyes based upon the implications of all these previous tests. The Committee accepted levelling or migrating (diffusion) power as the criterion of direct dye behaviour, and indicated how this property was influenced by the factors—temperature, liquor : goods ratio, and salt additions. The effects of the first two factors were covered by a general statement qualitatively true for all dyes. The effect of salt was used, alongside the intrinsic migrating properties, as a means of selecting dyes. In fine, the following was recommended—

Dyes should be subjected to—

(i) A test for migration power

(ii) A test for salt controllability.

They should then be classified as—

CLASS A—Dyes having good levelling or migration properties.

CLASS B—Dyes of poor levelling properties but which can be dyed uniformly by the controlled addition of salt to the dyebath.

CLASS C—Dyes of poor migration with which control by temperature as well as by salt is required.

Dyes from different groups should not in general be used in the same dyebath.

Now what is meant by "control" in Classes B and C is simply control of dyebath exhaustion. The "controlled addition of salt" means the gradual increasing of dyebath exhaustion with salt increments added over a period of the dyeing time during which the bath is exhausting at a smooth rate. "Control by temperature" means achieving a smooth rate of exhaustion by the use of gradually increasing temperature. This control of exhaustion is essential, because a too rapid exhaustion with dyes which do not level quickly means a bad strike, i.e. non-uniform surface adsorption; and the lower the levelling power of the dye the greater the time needed and difficulty experienced in correcting the strike by redistribution of dye. The Class A dyes are those which do level quickly; i.e. they are of such high diffusing power that a bad strike does not matter, because once adsorbed on fibre surfaces they rapidly migrate evenly into the mass being dyed.

### 3. MIXING OF DYES

The colourist can rarely achieve a required shade with a single dye; normally he uses two or three, and in binary and ternary mixings it will often happen that the relative concentrations are widely disproportionate, one dye often being present merely as a trace. If he uses dyes which exhaust at similar rates, he can control the course of dyeing; the change taking place with time is essentially that of increasing depth. If he has chosen dyes which exhaust at widely dissimilar rates, changes in depth and in hue are taking place at once.

Exhaustion rate is determined by two factors—salt sensitivity and diffusing power. There are lists of dyes in the literature showing how very widely both attributes vary from dye to dye. The Society's A, B, and C classification aims at a means of assessing these factors simply, and when we accept the dictum that dyes from one class should not be mixed with dyes from another, we are merely recognising the individual behaviour of dyes. In addition to this, it is worthwhile making finer distinctions within a given class, using published data to choose dyes which come as close together as possible with regard to diffusion constants and reaction to salt. The exigencies of fastness requirements, shade required, availability of dyes, and other factors all come into and restrict choice; but it is worthwhile exercising what choice there is on the principle that optimum compatibility means greater control over exhaustion, shorter time on the machine, and consequently more efficient use of heat and labour to produce dyeings of maximum uniformity and penetration.

## III—Modern Practice

### 1. PACKAGE DYEING

In the early days of viscose rayon, yarn was dyed in skein form by stick dyeing or on Gerber-type machines. It was soon realised that two major advantages would accrue from dyeing in a package system—firstly, the yarn would be in better condition for winding and processing generally; secondly, with the advent of the Topham box, viscose rayon yarn was spun into a ready-made package, from which it could after dyeing be wound into the required form. If it could be dyed in box-spun cake form instead of skein, a hank-winding operation would be cut out. Direct cotton dyes were the first class to be successfully applied to cakes of viscose yarn, and to-day less and less continuous-filament yarn is direct-dyed in any other form in this country. The principles of package dyeing are the same, whatever form the fibre to be dyed may take. Appreciating the fact that rayon staple, whether loose slubbing, tops, or

yarn, is also dyed in package systems, we might review those principles first in general terms.

In any package dyeing machine the material is static in a circulating dye liquor, forming a series of separate, highly swollen, dense packages, as with cakes and cheeses, or a solid, dense, equally swollen single mass in the case of packed fibre in loose sliver, top, or hanks. The dyer's task is to ensure that, when the overall appearance of his material matches his pattern, dye is uniformly distributed throughout the whole of the mass.

The driving forces behind the transference of dye from dyebath to fibre are— (i) the hydrodynamic pressure of liquor circulation, which distributes dye molecules throughout the mass; (ii) adsorption of dye by attraction to the fibre surfaces; and (iii) penetration of dye into the mass by diffusion into the fibres and along the layers of water between them.

These forces determine the rate of dyebath exhaustion. Often a very high degree of exhaustion is reached in the first few seconds of dyeing (due to (ii)), and it is thus not possible to distribute dye uniformly throughout the package before impoverishment of the dyebath has taken place.

If it were possible to avoid any exhaustion of the bath whilst distributing soluble dye throughout the package, there would be no problem. That is not possible; but it *is* possible for the dyer so to regulate exhaustion that the rate does not increase sharply at any point, and this must be the first aim in package dyeing. If uniform flow of dye liquor throughout the package could be so rapid that dye was uniformly distributed at a rate higher than that at which it was adsorbed on fibre surfaces, then, also, there would be no problem. This, too, is impossible with machines and packages as we know them. What the dyer has to do is to use the maximum possible rate of flow throughout and the minimum degree of bath exhaustion at the onset of dyeing. If the migration (levelling) properties of all dyes were such that dye could very rapidly transfer itself throughout the mass by diffusion, again there would be no problem. But the slowly diffusing dyes (Classes B and C) must be used for their hue and fastness properties, and the dyer has therefore to recognise the need for ensuring maximum uniformity of distribution of dye in the first place.

Thus the production of uniformly dyed packages is favoured by low dyebath exhaustion rate, rapid and uniform flow of dye liquor, and high diffusing rate of the dye itself. This last is largely out of the dyer's control, except that he should never use, in the same dyebath, dyes of widely differing diffusion rates. Regulation of liquor flow is a matter of the type and efficiency of the machine and the nature of the package and manner of arranging it in the container; these are only partly within the dyer's control. Exhaustion, in rate and in degree, is the one factor over which the dyer has more or less complete control, and the whole art of package dyeing depends upon how he exercises it.

### (*a*) *Viscose Rayon Cakes*

A pot-spun viscose rayon cake is a straight-sided hollow cylinder of tightly wound yarn, of total conditioned weight 1 lb.–1 lb. 4 oz. The overall diameter is 6½ in. and the annular width 1¼ in. In proper condition for dyeing it should have retained its geometrical shape, should be of uniform density throughout, and should show no sign of splitting at the annular edge to form telescopic moving sleeves. Cakes for dyeing together should be within an ounce or so of a standard weight and of uniform permeability. Such is the control now possible in viscose spinning that these desiderata are generally present in commercial lots. Further, the dye affinity of the yarn within a cake should be uniform. This may be affected by many of the steps in viscose manufacture. The viscose solution, the conditions of chemical precipitation, and the degree of stretch and orientation are obvious sources of possible variation. But all these are now capable of very fine control indeed.

The more likely sources of variation in dye affinity occur in cake-washing, where the yarn is freed from acid, salts, and sulphur, and in the drying, which needs to be carried out with great care. Many processors and dyers have in the past found for themselves that overdrying, on the one hand, and steaming, on the other (as e.g. in the setting of twist), can influence dye absorption in the direction of lowered affinity. In the first drying of freshly spun cakes the fibre is in a very swollen and reactive state, and must be dehydrated very gradually and uniformly if similar, permanent effects are not to be induced at the point of production. The present-day uniformity of 1-lb. rayon cakes in this respect is a tribute to the rayon industry.

At this point it should be mentioned that, in testing for uniform dyeing of his lot, the dyer should make knittings from one or two cakes of a little yarn from the outside, middle, and inside of the package. He can then see clearly the degree of unevenness. If he suspects that the yarn and not the dyer is responsible for this, his direct dye may be readily stripped with hydrosulphite, the three-panelled knitting redyed with a Class B or C dye, and the result observed. If the same unevenness persists, it is safe to exonerate the dyer.

Fineness of denier plays an important part in the course of dyeing. The finer the denier the lower the cake permeability, owing to closer packing of filaments, and therefore the slower the liquor flow through the cake structure in a given machine of fixed pumping capacity. In general this means that fine deniers are longer on the machine than coarse, for a given shade. This effect is partly offset by the fact that fine deniers, given equal access to dye liquor, level more readily than coarse because of the greater surface per unit weight. In addition, the finer the filament the greater the weight of dye required to give the same depth of shade on a given weight of yarn.

Three types of machine are available—
(i) Obermaier (ii) Longclose (iii) Courtaulds.

(i) In the first named, cakes are packed brick-wise in the perforated cage. Since dye liquor is not delivered to each cake individually, access of dye to yarn depends upon the regularity of packing and the shape and size of the inter-cake spaces. It is, therefore, inevitable that re-packing during the course of dyeing should be necessary, not once, but several times. This is expensive in labour, detracts from smooth control of exhaustion, and does not improve the condition of the yarn. This method of package dyeing box-spun cakes is to be strongly deprecated in favour of methods whereby there is a positive flow of liquor to each individual cake, as in the remaining two machines, in which the cakes are supported on a column or on holders.

(ii) The Longclose cheese-dyeing machine is too well known to call for any description here. The only adaptation necessary to the standard design is the provision of perforated Bakelite or stainless steel holders, on to which the annular cake fits snugly but not tightly. The loaded holders are stacked vertically, resting on each other along the vertical perforated spindle.

(iii) The Courtaulds machine, in use since 1941, has also been fully described elsewhere. Here the cakes are mounted on perforated tubes which carry 7 or 8 cakes each; the tubes are slid over perforated dye-delivery spindles in a horizontal position, so that each spindle is delivering dye liquor to a continuous sleeve of rayon, held in position by an adjustable nut at each arm end. It is an open machine of very simple construction and ease of loading; liquor flow is one way only, inside to outside.

Dyeing procedure designed to ensure exhaustion control is essentially similar in both Longclose and Courtaulds types of cake-dyeing machine; only dressing and entry into dye are different. In the former it has been found advantageous to enter the cakes dry. With the Courtaulds type, which is specially designed for rayon cakes, they are allowed to soak in boiling water for 10 min. before entering into dye. This procedure takes advantage of the fact that the cakes aligned on each arm, in contact with each other, swell on wetting to form a solid tube from a continuous sleeve. This arrangement is not possible on the Longclose cheese-dyeing machine, which, made to take all types of wound package, requires each cake to be separately supported on a former. There is no point in a pre-swelling treatment, and the advantage gained in entering dry, so that for a very brief few seconds dye liquor can more readily penetrate inside the unswollen cake, is utilised.

With most dyehouse waters a little Calgon T (Albright & Wilson) (0·25 part per 1000 of liquor) is advisable. In the Courtaulds machine this is added before pre-wetting, and the same liquor is used for dyeing.

The dissolved dye, with 0·125 part of Lissapol LS (ICI) per 1000 or, in the case of pale shades, 1 part of soap per 1000, is boiled up in the bath. If dyes are to be used which tend to lose value by chemical reduction on boiling, a small addition of ammonium sulphate should be made at the outset.

Dye liquor is circulated until the outside appearance of the cakes is uniform, usually up to 30 min., at which time they should be inspected. The controlled addition of salt is then begun. A concentrated solution of salt is drip-fed, the rate of feeding depending upon the class of dye and the depth of shade, as indicated below. The liquor : yarn volume ratio is 15–20 for the Longclose and 10–15 for the Courtaulds machine. The amount of salt (based on the weight of yarn) is predetermined by an accurate laboratory matching.

CLASS A DYES

| | |
|---|---|
| Light shades ... ... | 0·25% per hour |
| Medium shades ... ... | 0·5% per hour |
| Medium–heavy shades ... | 1·0% per hour |
| Very heavy shades ... | All the salt may be added quickly, and the dyeing boiled until level. |

CLASS B DYES

| | |
|---|---|
| Light shades ... ... | 0·25% per hour |
| Heavy shades ... ... | 1·0% per hour |

With Class B dyes, never more than 1·0% salt per hour should be added, and shades intermediate between the above limits should be salted with the minimum economic amount between the limits 0·25 and 1·0%.

CLASS C DYES— These are used, as far as possible, only for heavy shades. In that case, no advantage is gained in starting at a low temperature. Dyeing is at the boil throughout, and salt is drip-fed as with Class B dyes. When medium shades must be dyed, temperature control in the absence of salt, as in the Society's recommendation, followed by boiling with controlled salt addition, is essential. For pale shades, the most difficult to dye, there is rarely any point in using Class C dyes. This class has high wet fastness, and most demands in *pale* shades can be met with Class A and B types, generally the former.

For package dyeing on circulating machines, the concentrated dye brands should be used. With certain B and C types this is absolutely essential. The commercial standard brands often contain sufficient salt to create a bad strike during the initial half hour of "salt-free" dyebath circulation.

Dyeing should be followed by a fresh cold liquor containing 4 parts of Calgon T per 1000, and a softening agent, the concentration of which depends upon the demands of subsequent processing.

### (*b*) *Viscose Rayon Staple*

Compared with the dyeing of continuous-filament cakes, the time required to level-dye Fibro (Courtaulds) with the same dyes is much shorter, and the necessity for the control of exhaustion, though still essential, is less critical. Thus salt additions to Class A and B dyebaths may be much more rapidly fed, and it is *not* necessary to exercise temperature control with Class C provided salt control is adequately strict.

Loose Fibro should be dyed on the Obermaier-type machine, the cage of which is allowed to carry approx. 12·5 lb. per cubic foot capacity for deniers of 1½ and 3. For the coarser deniers, slightly bigger weights may be safely used.

The dry staple is entered into dye liquor at 95–98°C. containing 0·25 part of Calgon T per 1000, and the bath circulated for 10 min. Salt is then drip-fed, to the predetermined quantity, over a period of 30 min. Even with Class B and C dyes, a further 30 min. with the bath maintained near the boil is sufficient for uniform dyeing. It must be remembered that the very high degree of levelness called for in cakes is never justified in dyeing loose staple, which is to be carded and/or combed and of necessity interblended. The results of the salt-controlled direct dyeing of loose Fibro obtained in this way are generally superior in levelness to the traditionally satisfactory results obtained in the dyeing of loose wool, for example, Fibro being itself a more uniform material.

Fibro in sliver form may be direct-dyed in hanks on Obermaier machines, on circulating machines of the same type as those used by worsted slubbing dyers, or in top form on the Longclose machine. (As far as the author's experience has gone, can-type top-dyeing machines do not seem to have high enough positive flow rate to deal with the most difficultly levelling dyes.)

When dyed in hank, the directions are exactly as for loose staple, except that the packing of hanks is never so uniform as with loose staple and exhaustion should be controlled somewhat more stringently to avoid overdyed places due to channelling of the liquor. Dyeing should be allowed to proceed, at the boil, for 30 min. before salt is added, and the salt feed should be controlled by gradual addition over a period of 1 hr.

In top dyeing, the dyer may meet ball tops or Greenfield tops (made by direct conversion from tow). Both are dyed on the Longclose machine, mounting on the perforated spindle being facilitated by drawing out the centre of the top to give a 2 in. diameter central hole, the drawn-out sliver then resting spread on the upper top surface. A length of net is wrapped round the top to prevent damage. The bath is prepared as for loose Fibro or hanked sliver, and the tops are entered dry at the boil and dyed for 30 min. without salt additions. Because of the size (7 lb.) and the tightness of packing required to hold the top together, penetration is much more difficult than for any other form of staple package. This is met by extra control over exhaustion, and salt is drip-fed for 1–3 hr. The actual time required depends on class of dye and depth of shade, the salting rates varying in a similar manner to those laid down for cake dyeing. The flow of liquor is maintained from inside to outside.

*(c) Viscose Rayon Staple Warp and Continuous Tow*

Fibro warp and continuous tow are dyed on the Obermaier type of machine. The warp or tow is packed as evenly as possible into the perforated cage, so that an even flow of liquor is achieved without channelling. The material is entered dry into the dye liquor, the addition of salt being made by the drip-feed method. The rate of addition for warps is similar to that described for cake dyeing, whilst with continuous tow, where levelness is not of the same importance, salt is added as with loose Fibro.

### 2. HANK DYEING IN STATIC DYEBATHS

Hank dyeing is mainly practised on machines of the Sellars or Gerber type (without crank throw) (Europe) and the Smith Drum cascade type (U.S.A.), the hanks being carried on rotating rollers which move the yarn continuously in a static dyebath (Gerber) or a cascading bath (Smith Drum).

Using the Gerber machine, the following operational outline is sound practice—

Yarn is received in hanks generally weighing 2 oz., though up to 8 oz. can be dyed successfully. The number of hanks per roller is determined by the fineness of denier and the class of dyes used—

CLASS A DYES— Using 150 denier or coarser, 7½ lb. of yarn per roller may be dressed. The finer the denier the less the load should be, down to 3 lb. per roller for 75 denier.

CLASSES B AND C— Not more than 4 lb. of 150 or coarser denier should be dressed per roller, and 3 lb. for the finest deniers.

Liquor ratios can vary widely on this machine, but generally should be maintained at 40 : 1. Using highly salt-sensitive dyes of Classes B and C, especially in pale shades, some advantage is gained by increasing this, the limit being ca. 60 : 1.

The yarn is entered dry into the bath, containing a little Calgon T, which is maintained at a temperature as near the boil as possible. Salt is added progressively, the rollers being lifted during each addition to the bath. For dyeings requiring 10% of salt or less, the additions are in seven equal increments, the period of "down" between each addition being approx. 7 min. If greater than 10% is used, ten separate increments are usual. Between each "down" the liquor is brought to the boil. When using Class C dyes in heavy shades, three "downs" are given before salt additions commence.

Skeins of rayon take on a dense rope-like form during dyeing, and the operative dyer must see that these are kept as loose as possible by hand opening during dyeing.

Spun Fibro yarn may be dyed by the same method. There is a tendency for the air between fibres to become very effectively trapped as the yarn wets out; the skeins tend to float, leading to entanglement and consequent poor winding. Hanks of Fibro may be dyed by the same controlled technique as that used for loose staple, on the Obermaier principle. But provision of a homogeneously packed mass is a constant difficulty, and repacking of the hanks several times following inspection during dyeing is often called for, depending upon the class of dyes used.

### 3. DYES FOR VISCOSE RAYON

So much has been written about the properties of direct dyes that, armed with the Society's report and the full information now given by most dyemakers, any dyer should be able to make his choice of dyes intelligently and critically.

By making his selection according to known properties, the practical man is applying dyeing theory in its more vital phase. Just as he would not think of choosing a dye for a given purpose without reference to its fastness properties, so he should not consider its application by a given method without first knowing its dyeing characteristics. Published data will present these characteristics in a variety of forms for a very large number of existing dyes. Where that is not so, the Society's tests for classification into the three groups already discussed are very simple to carry out, and should be amongst the established testing and evaluation methods of every dyehouse. Many dyers go to great trouble to test incoming dyes for tinctorial value, shade, and fastness; it costs no more effort to test them for dyeing behaviour, and it is even more vital in the ultimate saving of heat, time, and materials.

The following tables are neither final nor comprehensive. They present classified groups of dyes which may be used in mixings and which will respond to the methods of dyeing discussed above to give level results for optimum time and effort when applied to any form of viscose rayon. To assist in selection for particular purposes, light fastness figures are given. As to wet and washing fastness, it is clear that the more slowly migrating the dye, the faster the dyeing; therefore direct dyes divide themselves broadly into Class A dyes, of low fastness, and Class B and C dyes, of relatively high fastness. But wash fastness depends so greatly on depth of shade that the dyer's own experience and needs, helped by the dyemakers' fastness figures, must be invoked for particular cases.

It is not possible to align washing and light fastness completely with the A, B, C Classification. Class A dyes are mainly used for the group known commercially as "ordinary dyes", but they are also used for suitable shades required in the grade known as "light and/or washing fast". For example, lingerie shades are not exposed to light and are usually so pale that even very self-levelling Class A dyes are sufficiently fast to water and washing. Even Icyl Orange RS has been used for many years for this purpose, although some doubts have been cast upon whether this is not going too far, even for this type of trade. Other pale shades can be obtained fast to washing with Class A dyes and are used for trades where light fastness is not required or is of minor importance. Likewise a few Class A dyes have good fastness to light, and can therefore be used in heavy shades where fastness to water or washing is not important.

When, however, fastness to washing is required in heavy shades, obviously Class B and C dyes must be used and, in the case of the heavier shades, must be aftertreated with Fibrofix–copper acetate, although it is possible to obtain a number by "soaping down". In general, the direct dyes which are fastest to light are to be found in Class B, although in addition to the exceptions named in Class A, there are also some Class C dyes of good light fastness. Class C dyes vary considerably in fastness, but by definition have the property of building up to considerable depth and are often cheapest for this purpose, e.g. Melantherine BH and Chlorazol Black E.

Another aspect of the matter which cuts across the alignment of the A, B, C Classification with fastness is that of hue. Chlorantine Fast Green 5GLL is a very useful self-green which it is difficult to imitate otherwise than by the use of blue–yellow combinations, and this factor combined with its brightness of shade will often lead to its use in the absence of a Class A green.

In the following annotated tables, light fastness on the S.D.C. scale (*B.S.* 1006) is the value as confirmed by the author and his colleagues. Those dyes marked with an asterisk tend to lose value by reduction on dyeing, and should be dyed in the presence of 0·5% ammonium sulphate.

### *Class A Dyes*

(Class B dyes which are used in the absence of suitable Class A dyes are placed in brackets.)

| *Colour Index* No. | Dye | Light Fastness |
|---|---|---|
| | (*a*) Lingerie Shades | |
| 324 | Diazo Brilliant Orange GR (FBy) ... | 3 |
| — | Icyl Orange R (ICI) ... ... ... | 3–4 |
| — | Chlorazol Fast Orange G (ICI) ... | 3 |
| 365 | Chrysophenine G (ICI) ... ... | 4 |
| — | Diazol Light Yellow 4J (Fran) ... | 5 |
| — | Benzanil Fast Yellow 5GLL (YDC) | 5 |
| — | Durazol Yellow 4G (ICI) ... ... | 5 |
| 278 | *Diphenyl Fast Red 7BL (Gy) ... | 4–5 |
| 319 | Durazol Helio B (ICI) ... ... | 4–5 |
| — | *Rigan Sky Blue G (CAC) ... ... | 4 |
| — | *Direct Fast Black B (CAC) for flattening when necessary ... ... ... | 4 |
| | (*b*) Blue Shades | |
| — | *Rigan Sky Blue G (CAC) ... ... | 4 |
| — | Chlorazol Blue G (ICI) ... ... | 3 |
| — | Chloramine New Blue 5B (S) ... | 2 |
| | Navy Blue Shades | |
| — | Icyl Blue 2R (ICI) ... ... ... | 4 |
| — | Icyl Blue G (ICI) ... ... ... | 3 |
| — | *Durazol Grey RG (ICI) ... ... | 3–4 |
| | Examples of dyes used for shading purposes are— | |
| 319 | Durazol Helio B (ICI) ... ... | 4 |
| — | *Durazol Grey RG (ICI) ... ... | 3–4 |
| 365 | Chrysophenine G (ICI) ... ... | 4 |
| | (*c*) Green Shades | |

These are divided into pale, medium, and heavy shades; but it will be realised that there must be considerable overlapping when the various other considerations of fastness, and the class of trade for which the shades are to be used, are taken into account.

| | | |
|---|---|---|
| | (*i*) *Pale Shades* | |
| ( — | *Chlorantine Fast Green 5GLL (CAC) (Class B) ... ... ... ... | 6) |
| ( — | Chlorantine Fast Green BLL (CAC) (Class B) ... ... ... ... | 6) |
| — | *Rigan Sky Blue G (CAC) ... ... | 4 |
| 365 | Chrysophenine G (ICI) ... ... | 4 |
| — | Diazol Light Yellow 4J (Fran) ... | 5 |
| — | Benzanil Fast Yellow 5GLL (YDC) | 5 |
| — | Durazol Yellow 4G (ICI) ... ... | 5 |
| — | *Direct Fast Black B (CAC) used for flattening ... ... ... ... | 4 |

| *Colour Index* No. | Dye | Light Fastness |
|---|---|---|
| | *(ii) Medium Shades* | |
| | As for pale shades and, with suitable yellows as above— | |
| — | Chlorazol Blue G (ICI) ... ... | 3 |
| | *(iii) Heavy Shades* | |
| | In the dyeing of heavy shades the Class C dyes Diphenyl Green 2G and Chlorazol Dark Green PL are used, where possible, as a basis for economic reasons. In cases of difficulty the more expensive Class A dyes must still be used. | |
| | *(d)* Gold, Yellow, Orange Shades | |
| 365 | Chrysophenine G (ICI) ... ... | 4 |
| — | Diazol Light Yellow 4J (Fran) ... | 5 |
| — | Chlorantine Fast Yellow 8L (CAC) ... | 6 |
| — | Pyralon Orange G (LBH) ... ... | 4–5 |
| | using dyes such as Durazol Red 2B and Direct Fast Black B for shading purposes. | |
| | *(e)* Pink and Red Shades | |
| | *(i) Pale to Medium Shades* | |
| 278 | *Durazol Red 2B (ICI) ... ... | 4–5 |
| — | Benzanil Fast Bordeaux 2BLN (YDC) | 5 |
| 353 | Chlorazol Fast Pink BK (ICI) ... | 5–6 |
| | with Pyralon Orange G, Durazol Helio B, and Direct Fast Black B as examples of shading dyes. | |
| | *(ii) Heavy Shades* | |
| | It is customary to use the borderline Class B dye Chlorazol Fast Red F (ICI) as a basis for heavy red shades for economic reasons. | |
| | Similar shading dyes are used as with pale to medium shades, another instance of mixing dyes from different groups. | |
| | *(f)* Grey, Fawn, Brown, Nigger Shades | |
| — | Pyralon Orange G (LBH) ... ... | 4–5 |
| 278 | *Durazol Red 2B (ICI) ... ... | 4–5 |
| — | *Chlorazol Fast Black BK (ICI) ... | 3–4 |
| | are commonly used as a basis for this class of shade. Chrysophenine G can be used for slight shading when necessary. | |
| | *(g)* Mauve and Helio Shades | |
| 319 | Durazol Helio B (ICI) ... ... | 4 |
| 319 | Chlorazol Fast Helio 2RK (ICI) ... | 4–5 |

## *Class B Dyes*

This class of dye is mainly used for fast-to-light and fast-to-light-and/or-washing shades. Heavy shades may require aftertreating with Fibrofix or may be soaped down.

| *Colour Index* No. | Dye | Light Fastness |
|---|---|---|
| | *(a)* Blue Shades | |
| — | *Chlorantine Fast Blue GLN (CAC) ... | 6 |
| — | *Durazol Blue 2GN (ICI) ... ... | 5–6 |
| — | *Durazol Blue G (ICI) ... ... (This dye is not used in conjunction with Fibrofix and copper acetate; Durazol Blue 2GN is used when necessary.) | 5 |
| — | *Solophenyl Blue 10GL (Gy) ... | 6 |
| | *(b)* Green Shades | |
| — | *Chlorantine Fast Green 5GLL (CAC) | 6 |
| — | Chlorantine Fast Green BLL (CAC)... | 6 |
| — | *Solophenyl Blue Green BL (Gy) ... | 6 |
| | This dye is used in conjunction with dyes such as— | |
| — | Durazol Orange 2G (ICI) ... ... | 6–7 |
| — | *Chlorantine Fast Blue GLN (CAC) ... | 6 |
| — | *Solophenyl Blue 10GL (Gy) ... | 6 |

| *Colour Index* No. | Dye | Light Fastness |
|---|---|---|
| | For heavy shades of some fastness to light, the following combinations can be used— | |
| — | *Durazol Blue G (ICI) ... ... ... | 5 |
| | with the following Class A yellows— | |
| ( — | Diazol Light Yellow 4J (Fran) ... | 5) |
| ( — | Benzanil Fast Yellow 5GLL (YDC) ... | 5) |
| ( — | Durazol Yellow 4G (ICI) ... ... | 5) |
| | *(c)* Gold, Yellow, and Orange Shades | |
| — | Benzanil Fast Orange ER (YDC) ... | 5–6 |
| — | Durazol Orange 2G (ICI) ... ... | 6–7 |
| — | Solar Orange RGL (S) ... ... | 5–6 |
| — | Solar Yellow 2R (S) ... ... ... | 7 |
| | These dyes are used as the basis for this class of trade. | |
| | *(d)* Red Shades | |
| 419 | Chlorazol Fast Red F (ICI) ... ... (This is used as a basis for heavy shades of ordinary fastness.) | 4–5 |
| — | Durazol Red 6B (ICI) ... ... | 6 |
| — | Durazol Rubine B (ICI) ... ... | 6–7 |
| — | Durazol Scarlet 2G (ICI) ... ... | 5–6 |
| ( — | Benzanil Fast Bordeaux 2BLN (YDC) (Class A) ... ... ... ... | 5) |
| — | Chlorazol Fast Scarlet 8B (ICI) ... | 3 |
| — | Sirius Scarlet B (FBy) ... ... | 5 |
| | *(e)* Grey, Fawn, Brown, and Nigger Shades | |
| — | Durazol Brown 8R conc. (ICI) ... | 7 |
| | The usual type of mixing for brown and nigger shades is— | |
| — | Solar Yellow 2R (S) ... ... ... | 7 |
| — | Durazol Orange 2G (ICI) ... ... | 6–7 |
| — | Solar Orange RGL (S) ... ... | 5–6 |
| — | Benzanil Brown 5RL (YDC) ... | 5 |
| — | Durazol Orange Brown 2R (ICI) ... | 6 |
| — | Benzanil Fast Orange ER (YDC) ... | 5–6 |
| — | Chlorantine Fast Blue GLN (CAC) ... | 6 |
| | The following dyes may also be used— | |
| — | Solophenyl Bronze BL (Gy) ... ... | 6–7 |
| — | Solophenyl Brown RL (Gy) ... ... | 6–7 |
| — | Solophenyl Brown GL (Gy) ... ... | 7 |

## *Class C Dyes*

These dyes are mainly, but not always, used when no high fastness is required. They are used chiefly in heavy shades for economic reasons.

| *Colour Index* No. | Dye | Light Fastness |
|---|---|---|
| | *(a)* Blue Shades | |
| 406 | Chlorazol Blue B (ICI) ... ... | 2–3 |
| ( — | Chlorazol Blue B 500 (Class B) ... | 2–3) |
| 401 | Chlorazol Black BH (ICI) ... ... | 3 |
| | *(b)* Green Shades | |
| 583 | Chlorazol Dark Green PL (ICI) ... | 3–4 |
| 594 | Diphenyl Green 2G (Gy) ... ... | 3–4 |
| | *(c)* Gold, Yellow, Orange Shades | |
| 814 | Diphenyl Chlorine Yellow FF (Gy) ... | 6 |
| 326 | Direct Fast Orange SE (CAC) ... | 4–5 |
| | *(d)* Red Shades | |
| 448 | Benzopurpurine 4B (ICI) ... ... | 1 |
| 495 | Chlorazol Purpurine 10B (ICI) ... | 1 |
| 326 | Direct Fast Scarlet SE (CAC) ... | 4–5 |

| *Colour Index* No. | Dye | Light Fastness |
|---|---|---|
| | (*e*) BROWN SHADES | |
| — | Durazol Brown 8RS (ICI) ... ... | 7 |
| 420 | Chlorazol Brown M (ICI) ... ... | 4 |
| — | Chlorantine Fast Brown BRLL (CAC) | 6 |
| | (*f*) BLACK SHADES | |
| 581 | Chlorazol Black E (ICI) ... ... | 3 |

## IV— Future Needs and Trends

With viscose rayon itself, any future developments will involve the fineness of denier, improvement in permeability of cakes, and, at longer range, production of packages other than box-spun cakes processed from continuously spun (Triple A) yarn, and extension of the spun-dyed (pigmented spun-dyed) range of shades. None of these factors will have a telling influence on what has been said in the body of this paper. The one certain trend is away from hank dyeing; there is so much in favour of package systems and it has already been said. As to spun-dyed viscose, spun as staple and continuous filament, the range will increase only as suitable fast pigments can be found. The chemical properties called for in the viscose spinning process are such that they are likely to remain restricted to certain classes of coloured pigment. But even were this not so, the necessity to spin white yarn and dye afterwards will always remain, because of the rapidly changing demands for fashion shades on the one hand, and the impossibility of colouring and spinning non-continuous small weights of variously pigmented yarn or fibre on the other.

The biggest recent development in extending the textile use of dyed viscose rayon staple has been its rapidly increasing use for blends with wool, i.e. fibre blends. This has shown the need for more direct dyes which are fast to milling and scouring and of relatively high light fastness. These considerations have been discussed at length elsewhere, but one or two points are worth emphasising.

Whilst vat dyes and sulphur dyes are bound to be used extensively for Fibro destined for suiting and hosiery yarns, direct dyes will take a great share in the inevitable increase in this development.

Recently the author made a study of all available ranges of dye for the production of suiting and hosiery shades on Fibro for blending with dyed wool. The shades chosen were fully representative of manufacturers' ranges. Taking everything into account— brightness of shade, fastness to milling, and fastness to light— vat dyes and sulphur dyes each failed in only one instance to match up to the fast dyed wool component. With direct dyes the following was found for eight suiting and eight hosiery recipes—

| | Suitings (8 fundamental shades) | Hosiery (8 fundamental shades) |
|---|---|---|
| Satisfactory matchings for hue, brightness, and depth ... ... ... | All | All |
| Fast to light ... ... | All | All |
| Fast to milling ... ... | 5 | 6 |

Thus, so long as direct dyeing has a price advantage over vat and sulphur dyeing, there should be a large proportion of Fibro, for the worsted trade, dyed direct.

The above results were possible using ordinary direct dyes aftertreated and copper-complex direct dyes.

The range was filled up by direct dyes aftertreated with Fibrofix and copper acetate, or Cuprofix, and the Cuprophenyl (Gy), Coprantine (CAC), and Resofix (S) dyes. It is significant that the milling fastness and light fastness called for could be obtained in a high proportion of cases with normal direct dyes, for the aftertreatment of which there exist several products, among which we have found Fibrofix generally effective.

With regard to the application of Coprantine, Cuprophenyl, and Resofix dyes to viscose rayon more generally, it has to be said that, as direct dyes go, they are expensive. Wherever an ordinary direct dye can be used in conjunction with Fibrofix (with or without copper acetate), Sandofix (S), Cuprofix, or any similar agent, these are a cheaper proposition. However, copper-complex dyes are an important attempt to fill a gap. Direct dyes which are fast to light and washing and build up well to give heavy shades are most certainly needed, and those possessing the last two attributes fall into Class C almost by definition. If the makers could produce them with the minimum sensitivity to electrolytes, as compared with the general run of Class C dyes, they would make a very important contribution. The copper-complex dyes, expense apart, do not themselves provide a complete answer, since they cannot generally be built up to very heavy shades and they lack certain bright colours at present.

In the direct dye ranges there is a general need for fast-to-washing reds, red–oranges, red–browns, and violets and for more dyes of similar light fastness to the well known Durazol Brown 8R (ICI) and Solophenyl Brown 8RL (Gy).

In dealing with dyes of high wet fastness, we are concerned with Classes B and C (slowly migrating). A great bulk of Class A dyes is, and always will be, used on viscose rayon, and here the needs are clear and urgent. We know of no Class A browns and greens, and were either available it would find immediate application in very considerable bulk.

Apart from the increasing use of rayon staple alongside wool, where high light and wet (milling, scouring, and washing) fastness is called for, there is a general move in the direction of higher fastness requirements for dyed viscose rayon. This results in part from a real demand for better quality by the consumer, from the acceptance of laid-down specifications, and from the extending uses to which rayon is being put. These latter include such widely different end-uses as brace webbings and carpets, which are mentioned because in both trades we have been asked by some manufacturers for higher fastness standards than are readily attainable with the general run of ordinary dyes. The increasing use of rayon in furnishings and

outerwear, such as tropical suitings, is having a marked influence on fastness requirements.

To sum up; if direct dyes are not to give place more and more to vat, sulphur, and azoic types, as the uses of viscose rayon expand, dyemakers' ranges must be reinforced with members of higher wash and light fastness, particularly reds and near-reds. There is no advantage to the dyer or the consumer in using expensive methods of fast dyeing when fast dyeing is not called for. For a number of trades the cheaply applied Class A "ordinary direct" dye is good enough, and we should keep some perspective in calling for higher fastness standards. Of that class the urgent need is for browns and greens and more greying and drabbing colours.

Taking a much more forward view, we might enquire into the possibility of entirely new types of direct dye, if by direct dyeing we mean the simple application of a substantive, coloured, plain-water solute. At present they are invariably sodium sulphonates of azo compounds of high molecular weight behaving as colloidal electrolytes. We now know why this type of compound behaves as a dye; which means that we know what attributes to look for in any other possible structures. Can rod-shaped, coloured compounds of high hydrogen-bonding capacity be based on any other than a benzenoid azo structure? Since highly conjugated structures are essential to the existence of colour, there may be no other possibility beyond benzenoid patterns. Whether that is so or not, do these structures need of necessity to be electrolytes and, in particular, metallic salts? If dyes could be solubilised in such a way that they were substantive yet not dependent for their affinity on dyebath electrolytes, we might see an end to the dyer's chief difficulty, that of controlling dye distribution throughout his fibre mass in whatever form it be. On the other hand, the fact that direct dyes as we know them *can* be controlled in their dyeing behaviour *at all* derives from this very dependence on electrolytes. The principal lesson in this paper has been to point to the necessity for that control and to show that it can be successful with direct dyes as we know them. So perhaps we should be satisfied with what we have, but at the same time we can utter a final plea to the makers to fill the existing gaps and extend the range in keeping with the uses to which viscose rayons, both staple and continuous, are being increasingly put.

* * *

The author's thanks are due to a number of his colleagues, especially Messrs. J. S. Ward, H. Hampson, S. Burgess, and E. R. Lambie, for assistance in the preparation and checking of the paper. He wishes to record his thanks to the Directors of Courtaulds Ltd. for permission to publish it.

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## Discussion

Mr. M. R. FOX: Is any significance to be attached to the fact that in Fig. 2 Benzopurpurine 4B has the *trans* configuration, while in Fig. 3 it has been given the *cis* configuration? Is there any experimental evidence to show that a *trans–cis* change of this type can and does take place?

Mr. BOULTON: Whilst the configurations of Benzopurpurine 4B are shown differently in Fig. 2 and 3, no significance is attached to this difference as the two forms appear to be interchangeable.

Mr. J. S. WARD*: The change of configuration involved here cannot be described as a *cis–trans* or *trans–cis* type of change. All that is involved is a simple rotation of one half of the molecule about the single bond joining the two halves. It has been shown that 2:2′-derivatives of benzidine similar to Benzopurpurine 4B, in which free rotation around this bond is not possible, do not yield substantive dyes. In preparing these diagrams, we simply utilised, from the point of view of presentation, the property of free rotation of the two halves of the molecule with respect to each other which appears common to all 3:3′-benzidine dyes.

Mr. T. FLANAGAN: The author states that, in viscose cake dyeing, never more than 1% salt per hour is added to the dyebath. Some dyes need appreciable amounts of salt to produce economic exhaustion of the dyebath, in many cases 7% or even more being necessary even for medium shades. Therefore, how long does it take to dye a Class B or C dye on to a viscose cake?

Mr. E. R. LAMBIE: It is correct to assume that, should it be necessary to add 7% salt, it would require 7 hr. dyeing time. This may appear to be excessive, but the stated rate of salting has proved to be the only method for obtaining satisfactory results with Class B dyes. It may be of interest to point out that a laboratory matching recipe may specify 7% salt, but owing to the longer time of dyeing with bulk lots in the works the actual amount of salt used would possibly be only 3–4%. Most Class B dyes reach about 70–80% exhaustion with this amount of salt when dyed in a liquor ratio of 12 : 1, as we usually do in bulk lots.

Mr. FLANAGAN: In the tables Durazol Brown 8R is classified in one case as a Class B dye and in another as a Class C dye. This must surely be an error.

Mr. S. BURGESS: This is correct, since Durazol Brown 8RS, as correctly stated in the I.C.I. publications, is a Class C dye, but when concentrated brands are available these approach or actually come within Class B.

With reference to the description of Solophenyl Brown GL as a salt-sensitive dye, attention should be called to the fact that there is some confusion here which was specifically disclaimed in the Society's report[1], where it is pointed out that such Class B dyes should be described as *salt-controllable*. Class C dyes could, in the speaker's opinion, be more properly described as "salt-sensitive", since

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they respond most readily to a small stimulus, viz. a small addition of common salt.

Mr. H. A. TURNER: We must lament the difficulties in which the yarn dyers place themselves through using too much water with their dye. It seems to me that pack dyeing, whether of large wound packages or of packed skeins or ball warps, while it maintains the yarn in good condition during prolonged dyeing, represents the very worst arrangement of the goods with which to meet the problems which arise when dealing either with dye application classes which are difficult to disperse, or with those in which the members show wide differences in rate of dyeing, salt sensitivity, etc. The piece dyer has found, whether it be in padding methods of the orthodox kind, or in the Standfast method, the value of rapid application of short dye liquors, with the distribution governed once and for all by the mechanical conditions of the nip or its equivalent. Here the dye has access to the yarn arranged in thicknesses of not more than one or two ends deep. The immediate analogue would be the padding of a sheet of yarn passing from beam to beam, and this brings other serious difficulties in its train. It seems, however, that single-end dyeing to make use of the idle time occupied in winding should be considered more carefully. The idea does not fit well into the present sequence of yarn handling, processing, and utilisation, but if it is not looked into here, it may well be taken up in countries where, because of vertical organisation, the sequence of processes is not so rigid as our own. The continuous methods of viscose spinning have shown that the mechanical problems inherent in the continuous wet processing and drying of separated ends of yarn are by no means insuperable. We should not be deterred by present conditions from looking into these possibilities. Some of the results of such an investigation might be unexpected and even disconcerting, but they would make a valuable addition to our present knowledge.

Mr. BOULTON*: In general, I agree. The threadwise continuous dyeing of the yarn would be a commonsense method, and investigations into technical possibilities are going on. It must be clear, however, that in these times of rapid development one cannot advocate the rendering obsolescent of established dyeing machinery without taking very careful thought indeed of the implications for fibres of many types. In short, this development is already in mind, but in its nature must be slow to reach its testing time. Investigation into continuous threadwise dyeing is not likely to produce much new basic knowledge of the mechanism of dyeing; such studies should surely be directed toward trying to establish whether or not it could be done economically.

Mr. A. S. FERN: What is the reason for the apparent paradox that (i) addition of common salt reduces the $\zeta$-potential and hence permits a greater equilibrium adsorption of dye anions by cellulose, and (ii) addition of common salt increases aggregation of the dye anions, thus reducing the concentration of single dye anions and hence lowering the equilibrium uptake, since only the unaggregated ions are adsorbed by cellulose?

Mr. BOULTON: The general equilibrium conditions in the direct dyeing of cellulose can be expressed as—

$$\text{Larger dye aggregates} \overset{(1)}{\rightleftharpoons} \text{Smaller dye aggregates} \overset{(2)}{\rightleftharpoons} \text{Dye absorbed by cellulose}$$

The smaller dye aggregates are those which can take part in the dyeing process; their maximum size is not known. Increase of salt concentration moves equilibrium (1) to the left and equilibrium (2) to the right. Increase of temperature has the opposite effect. It must be assumed that increase of salt concentration always has a greater effect on equilibrium (2) than on equilibrium (1), since all available evidence shows that such an increase is always accompanied by an increase in equilibrium absorption of dye.

Mr. FERN: The assertion that the source of the negative charge on the surface of the cellulose fibre in water is the presence of carboxyl groups is oversimplified. In general, even inert substances like hydrocarbons and glass are associated with a negative $\zeta$-potential when in contact with water, and presumably in cellulose a portion of the charge can be attributed to this phenomenon.

Mr. BOULTON: The theoretical part of the lecture was intentionally simplified in order to emphasise a few important points. However, the effect mentioned probably does contribute to the $\zeta$-potential of cellulose. But what may possibly be the major contribution is that due to the dye anions themselves. The absorption of a single dye anion may involve, at the same time, the absorption of four units of negative charge. The charge built up in this way can behave in a precisely similar way to the original negative charge of the undyed cellulose.

Mr. R. K. FOURNESS*: Is not the negative charge on the cellulose fibre during dyeing an example of the general rule that, when two substances are in contact, the one with the higher dielectric constant assumes the positive charge? Water, having a relatively high dielectric constant, therefore usually becomes positively charged towards most textile fibres immersed in it.

Mr. K. MCLAREN: The negative charge on cellulose is overcome by the addition of salt, which also causes aggregation of the dye. Have any experiments been made to ascertain if this charge could be overcome by the adsorption of surface-active agents?

Mr. J. S. WARD*: In the presence of a cation-active auxiliary such as Fixanol C (ICI) or after treatment with such an auxiliary, cellulose can be dyed with electrolyte-free direct dyes (without addition of salt). However, direct dyes themselves react with such auxiliaries to form water-insoluble complexes (hence the use of the latter in improving the water fastness of direct dyes). Therefore, although the cation-active agent may have overcome the negative charge on the cellulose, dyeing may have taken place by a mechanism differing

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from that of ordinary direct dyeing, namely reaction with absorbed cation-active agent rather than with cellulose itself.

Dr. H. R. HIRSBRUNNER: It is generally known that by means of air bubbling the overall rate of dyeing is considerably increased[2]. This is undoubtedly due to a great degree of liquid circulation, and therefore a more effective distribution of dye molecules on the fibre surface is achieved. This method would reduce the time of dyeing and increase levelness. Has any practical device of air bubbling ever been considered?

Mr. BOULTON: Air bubbling is one more method of increasing the movement of dye molecules relative to the fibre. We have not attempted to develop a specific method of dyeing involving air bubbling, but we have studied the increase in rate of movement of dye liquor relative to fibre package in general terms. The use of bubbles (underwater explosions), vibrations of supersonic and sonic frequencies, and extremely high rates of liquor flow are all methods of increasing turbulence. If one dyes in a system such that the movement of liquor relative to fibre may be represented as streamline flow, bombardment of fibre surfaces by dye molecules or particles is bound to be very slow as compared with a system in which there is some turbulence. In an efficient machine turbulence probably exists, and the question is simply how it is achieved and to what extent it is useful to increase turbulence beyond a certain point.

Mr. R. K. FOURNESS*: How is the improved wash fastness of direct-dyed cellulosic materials when aftertreated with, say, formaldehyde or one of the cation-active substances explained in terms of the theory of dyeing outlined in the paper?

Mr. BOULTON*: The mechanism of aftertreatment of certain direct dyes with formaldehyde to improve washing fastness has been discussed by Whittaker[3], who agrees that the improvement is probably due to an increase in molecular size resulting from union of two dye molecules by a methylene link. The compound will have a much lower rate of diffusion, and thus a better washing fastness, than the original dye.

Cation-active substances of low molecular weight have little beneficial effect on the washing fastness of direct dyes, but do improve the fastness to water and acid cross-dyeing. This improvement is apparently due to the formation of a water-insoluble complex between dye and cation-active agent of greater molecular size than the original dye. The water-insolubility and increase in size can both contribute to a reduction in rate of diffusion. In soap solutions, however, the complex is unstable, and the diffusion rate of the dye assumes normal proportions.

In the case of complex-forming agents of high molecular weight such as Fibrofix (Courtaulds), however, which are of the resin type and are not normally regarded as cation-active, the complex is stable towards soap solutions, and treatment with such agents improves the washing fastness of direct dyes.

Mr. E. STEAD*: How far can current theory be applied to the application of vat dyes, which often have no obvious rod-like structure, particularly in the Standfast molten metal machine, where the time of dyeing is so different from that used in the older types of machines.

Mr. BOULTON*: The advantages of the Standfast molten metal machine for application of vat dyes can be stated in terms of dyeing theory as follows. Uniform distribution of dye is controlled mechanically by impregnation of fabric with dye solution in its brief passage through the dye liquor and expression of excess solution upon entry into the molten metal. In this way the advantages of the pigment padding process are obtained. The rate of diffusion of dye into fibre is increased many times, compared with normal dyebath conditions, by the high temperature of the metal and the very short liquor ratio. (All the liquor involved is that held by the fibre.) Thus the advantages of steaming conditions, with better heat transfer (due to the high specific heat of the metal) and with complete absence of air, are obtained.

Mr. J. S. WARD*: Current dyeing theory recognises little difference between vat dyes and direct dyes. To quote from a recent paper[4]—

> Dyeing of cellulose with vat dyes proceeds in the same manner as dyeing with direct dyes, involving adsorption of anions, and the distribution of sodium ions between fibre and liquor obeys the laws of membrane equilibrium. The differences between vat dyes and direct dyes in their practical behaviour seem, therefore, to be based mainly on the high electrolyte content of a normal dyebath.

Boulton and Morton[5] introduced their original studies of vat dye diffusion in viscose rayon by stating that the process was fundamentally the same as the absorption of direct dyes.

### References


[1] "Report of the Committee on the Dyeing Properties of Direct Cotton Dyes", reprinted from J.S.D.C., **62**, 280 (1946).

[2] Rendell and Thomas, J.S.D.C., **51**, 157 (1935).

[3] Whittaker, J.S.D.C., **63**, 179 (1947).

[4] Fowler, Michie, and Vickerstaff, *Melliand Textilber.*, **32**, 296 (April 1951).

[5] Boulton and Morton, J.S.D.C., **55**, 481 (1939).


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# A Practical Survey of Hosiery Dyeing

W. A. Edwards

The survey is intended to indicate how advances in hosiery-dyeing techniques have been made possible by technical developments in dyes and auxiliaries. In tracing these developments from the use of natural dyes in the later nineteenth century to representative modern practice, the practical application of scientific method and control is discussed with the more important theoretical advances in mind. Following a discussion of special considerations in the dyeing of knitted footwear and fabrics by different methods, recently developed features of hosiery-dyeing machinery are outlined.

## INTRODUCTION

In the first place, it has been considered preferable, for the purpose of this survey, to limit the interpretation of the word "hosiery" to cover only the knitted footwear and tubular fabric sections of the trade, since together these probably constitute the major portion of the knitwear industry as it is known to-day.

The most important feature of a knitted material is its ability to stretch in length and breadth. Even with a similar yarn, by making alterations during the knitting operation one can produce articles and fabrics of widely differing characteristics. Whilst these modifications may be principally mechanical, it is important to stress the physical and chemical considerations which must be taken into account whenever "wet processing" is contemplated, whether this involves a preliminary scour, the application of a special finish, or a conventional bleaching or dyeing process.

Much has previously been written [1–5] regarding developments in the dye industry. Notably since the latter part of the nineteenth century, the number of commercially available dyes and auxiliaries has increased considerably, and new types have been evolved. At this juncture, an account may be given of the more important phases of development, both theoretical and practical, which have enabled the hosiery-dyeing industry to meet varied and more exacting consumer requirements with the passage of time, e.g. an increased demand for dyeings of superior light and washing fastnesses. It should be mentioned that in the early days the standards were necessarily arbitrary, but valuable guidance was afforded by the dye manufacturers, who compiled fastness tables for inclusion in their pattern cards. Since that time, much more information has been obtained from various sources and correlated by several bodies, notably the Society of Dyers and Colourists [6,7], Textile Institute, British Standards Institution [8], the various textile and allied Research Associations and Government Service Departments in this country, and by the corresponding bodies abroad.

## TECHNICAL DEVELOPMENT

Prior to 1900, shades required to be dyed on hosiery were, by fashion, met by the use of natural dyes frequently mordanted on the fibre. For example, logwood [9] was dyed on a chrome mordant for navy blues and blacks on wool, whilst fustic, similarly dyed, was used as the yellow component for browns and tans. Recipes typical of a few of these older methods include—

COTTON HOSE— BROWN

6th January 1874

50 lb. of goods—

| | | | |
|---|---|---|---|
| 20 lb. | ... | Cutch | 1 hour |
| 2 lb. | ... | Bluestone | |
| 1 lb. | ... | Logwood | |
| 1 lb. | ... | Salt | |

Blow off and beat for ¼ hour in ¼ lb. chrome water nearly boiling hot. Rinse well and then return to original liquor and again chrome, as before.

COTTON HOSE— DARK CHOCOLATE

6th March 1876

128 lb. of goods—

| | | |
|---|---|---|
| 48 lb. | ... | Redwood |
| 4 lb. | ... | Logwood |
| 3 lb. | ... | Cudbear |
| 1 bucket... | | Fustic |
| 3 lb. | ... | Bluestone |
| 1½ tots | ... | Sours |
| 2 lb. | ... | Tartar |

Boil bags for 1 hour and goods for 2 hours.

Sadden—

| | | |
|---|---|---|
| 12 oz. | ... | Copperas |
| 1 lb. | ... | Cudbear |
| 12 oz. | ... | Bluestone |
| ½ pint | ... | Spirits of salts |

About ¾ hour on to shade.

WOOL HOSE— SHIPPING OR BLUE BLACK

ca. 1880

First machine—

| | | |
|---|---|---|
| 1½ lb. | ... | Bichrome |
| 1 lb. | ... | Oxalic acid |

Boil for 1 hour, rinse, and blow off.

Second machine—

| | | |
|---|---|---|
| 3 lb. | ... | Alum |
| 3 lb. | ... | Tartar |

Boil for 2 hours, rinse, and blow off. Dye with 48 lb. of Logwood, Saline, and sours.

CHILDREN'S OR LADIES' HOSE— TAN

ca. 1900

Sweet chrome mordant

| | | |
|---|---|---|
| 7% | ... | Fustic extract |
| 7% | ... | Indigo extract paste |
| 2¾ pints % | ... | Orchil liquor |

MEN'S HALF HOSE— NAVY

ca. 1900

Sweet chrome mordant

| | | |
|---|---|---|
| 2½% | ... | Fully oxidised Hematine crystals |
| 1½ pints % | ... | Orchil liquor |

Since 1856, the year of Perkin's famous discovery of Mauve, the rapid developments in all branches of synthetic dye manufacture about 1890 had a noticeable effect on hosiery dyeing. Probably the first use of synthetic dyes was in combination with

natural dyes to obtain bright shades, otherwise unobtainable. Blues of the Patent Blue and Cyanole type began to compete with Indigo extract, and the earlier acid blacks were being tested in comparison with logwood. By 1900, improved acid dyes of the hydroxyanthraquinone type became available, and also azo dyes derived from salicylic acid. These could be dyed as acid dyes, and by aftertreatment with sodium or potassium dichromate their fastness properties greatly improved. The Berlin Aniline Co.[10] patented the metachrome mordant method of dyeing, also in 1900, and following its successful development by several dye manufacturers, notably Sandoz Ltd., a wide range of shades became possible.

In the early 1920s, the Society of Chemical Industry in Basle (now Ciba Ltd.) successfully developed the Neolan dyes, incorporating chromium in complex form in the dye molecule during manufacture. Thus it became possible to dye wool to very fast shades by a single-bath method similar in principle to that used for normal acid dyes. These innovations proved to be very valuable to the hosiery dyer.

In the early part of the present century, considerable interest was shown concerning the nature of dyeing processes. Thus began the studies which culminated in the first theories of dyeing, essentially theoretical yet supported by experimental and practical work. F. L. Goodall in 1935 classified wool dyes into the crystalloidal (molecularly dispersed) and colloidal (aggregated) acid dyes according to their state in solution [11]. It was thus made easier to distinguish between those dyes requiring to be dyed from an acid bath and those applicable from a neutral one. The latter type, however, gave uneven dyeing on hosiery on account of their poor levelling properties. For this reason, Goodall [12] proposed that dyeing should be begun at boiling point and that condition maintained. Appreciating the need to avoid too rapid exhaustion, he also proposed to decrease temporarily the affinity of the dye for the fibre, by commencing at a slightly higher pH obtained by the use of ammonia with ammonium sulphate in the dyebath. The technique of retarding the rate of dye absorption by the fibre has since been investigated further; in the case of dyes applicable from an acid bath, the importance of pH control has been emphasised notably by the work of Noble published in 1944 [13], and the use of phosphoric acid for this purpose has been patented [14]. Alternatively, ammonium dihydrogen phosphate may be used in a manner analogous to Goodall's ammonium sulphate technique. A paper by Ris *et al.*[15] introduces graphical representation of the dyeing properties of acid wool dyes; and the Report of the Wool Dyes Committee [16] proposes the adoption of standardised conditions and tests for examining the dyeing characteristics of wool dyes. Applications of the Report have been discussed by Kramrisch [17].

A theory has been established that dyeing takes place by rapid adsorption at the surface of the wool fibre, followed by migration from the surface to the centre, the second stage being relatively slow. Under usual dyebath conditions, boiling promotes even diffusion. However, greater evenness in initial adsorption may be obtained by careful pH control during dyeing; and the practical importance of this has been brought out recently by Lister [18].

During the past ten years other successful dyeing methods have been developed with the same idea of retarding the initial dye adsorption. A recent I.C.I. patent [19] covers the use of a suitable assistant in the dyebath during the application of selected neutral-dyeing dyes, including the Carbolans, by a modified technique. The boric acid process, patented by W. E. Saxby (Nottingham) Ltd.[20], provides a convenient method of equalising the pH condition of the wool before and during dyeing, and it is claimed that the amount of damage sustained by the wool is minimised by adopting conditions such as these. In the Wolsey process [21], after initial dye adsorption at low temperature, penetration and fixation are achieved by a subsequent steaming treatment.

In view of the widespread application of some form of shrink-resist treatment to wool, an assessment has been made of the fastness of acid, neutral-dyeing, and chrome dyes on wool, and of certain direct cotton dyes suitable for wool dyeing, to five commercial non-shrink processes, the results being presented in tabular form on a conventional 1–5 scale by the Clayton Aniline Co. in two circulars [22].

In the early years the synthetic direct cotton dyes available produced a limited range of shades, somewhat thin and unattractive compared with the fuller rich shades from basic and natural dyes. Great strides were made in the development of azo dyes, and A. G. Green's discovery of Primuline in 1887 introduced the technique of diazotisation and development, enabling a variety of shades, including orange, red, maroon, and purple, to be produced from the bright primrose-yellow dyeing on cotton. Recipes exist indicating use of these dyes on knitted materials as early as 1888. Although the light fastness of the developed dyeings was not very high, efforts were made to increase the range and to overcome this defect.

It was known that the light fastness of certain direct dyes was improved considerably when they were aftertreated with copper salts. With the Sky Blue FF type, however, the copper taken up during aftertreatment was removable by repeated washing. The Benzo Fast Copper dyes (Bayer) were first introduced as a range of direct dyes which yielded good fastness to light and washing on aftercoppering. The most recent developments have included the incorporation of quaternary ammonium compounds and synthetic resins, e.g. Fibrofix [23] and diamine–formaldehyde complexes [24], with the copper salts. In some cases, the appropriate dyes suitable for aftertreatment with a particular product have been grouped accordingly, and are now available as, for example, the Coprantine (Ciba), Cuprofix (S), Resofix (S), and Cuprophenyl (Gy) ranges. Coprantex A (Ciba) and Resofix VF (S) have recently been introduced as aftertreating agents.

A special committee of the Society has published its reports on the dyeing properties of direct cotton dyes [25], and the value of its efforts is well known. Boulton [26] and Lemin, Vickers, and Vickerstaff [27] have contributed considerable data of practical importance concerning the rates of dyeing. Thus the significance of temperature and salt control, and of rates of migration, have been studied with a view to defining accurately the behaviour of a large number of dyes under standard conditions. A novel feature was the presentation of this type of information in graphical form by the Geigy Co. Ltd.[28].

The water-soluble Ionamine range of cellulose acetate dyes was introduced following Green and Saunders' investigations in 1922. It was subsequently found that simple amino derivatives of anthraquinone in colloidal suspension produced shades of better light fastness on cellulose acetate materials, and these, together with some azo derivatives, are suitable for acetate rayon and some of the newer fibres, e.g. nylon and Terylene.

## PRACTICAL CONSIDERATIONS

With the advance made in the construction of hosiery machines in the early twentieth century, the manufacturer was afforded the opportunity of experimenting with finer-gauge hosiery and the incorporation of novel effect threads.

Developments in the manufacture of regenerated cellulose rayon rapidly advanced, but owing to various difficulties, e.g. the loss of strength on wetting, prejudices were many and the use of rayon was somewhat restricted. Later, manufacturers realised the potentialities of this fibre for ladies' hose and in conjunction with cotton or wool, probably introducing the first mixture of natural and artificial fibres requiring some special consideration during dyeing.

Because of the diversity of knitted articles, which may be made of the same fibre or of fibre mixtures, it is convenient to consider the dyeing of these sectionally, thus—

(1) Men's half hose
(2) Boys' and girls' three-quarter hose
(3) Children's sox, and ladies' ankle or tennis sox
(4) Ladies' hose, excluding those manufactured from nylon, outside the scope of this survey
(5) Knitted fabrics—underwear, sportswear, and outerwear.

## MEN'S HALF HOSE

In recent years, the principal developments have involved structural types. At the present time, the proportion of all-wool 6/3 168-needle (4 in. diameter cylinder) and other ribbed styles to the plain knit has increased considerably. A recent development consists of nylon toe-and-heel reinforcing yarn. The incorporation of cotton-covered rubber thread is a common feature of the short 6/3 half hose favoured in some markets. In many cases, some form of shrink-resist treatment is applied. It is important, therefore, that due consideration is given to the effect of any treatment on all the different fibres present.

In practically all instances, the dyes must be of good wet fastness, particularly to washing, e.g. S.D.C. Washing Test No. 2 [7]. Principally, chrome dyes are used—metachrome, afterchrome, or Neolan, but in the case of the brighter shades it may be desirable to use the acid milling or neutral types of dyes.

With this hosiery of complex knitted structure, it is necessary to ensure that all portions of the half hose are thoroughly penetrated in the previous scouring operation. From the latter, absorbed alkali may be distributed unevenly, and if a chlorination process precedes dyeing, any residual acidity would also affect the rate of dye absorption. Thus it is most important to level out these inequalities before dyeing, in order to achieve good heel-and-toe penetration. In particular, when dyeing by the afterchrome method, the addition of dichromate should be made only after ensuring satisfactory penetration of the goods and complete exhaustion of the dyebath. With the exception of producing dark browns and navy blues more economically by the afterchrome method, the metachrome technique is of particularly wide application for lighter shades. Since the dyeing is carried out under practically neutral conditions, shading is readily possible with either chrome or neutral-dyeing acid dyes. Where goods have been treated for shrink-resistance, careful selection of dyes is necessary, and a modification of dyeing technique may prove advantageous, in order to obtain level results on the modified fibres. If nylon is present as heel-and-toe reinforcing yarn or as a mixture with the wool, solid shades may also be obtained through the use of carefully selected combinations of the faster wool dyes; e.g. Polar Grey BL (Gy) yields solid shades on wool–nylon, and its wash fastness is comparable with that of chromed dyes. If desired to improve solidity through the additional use of disperse acetate dye, it is preferable to apply the requisite amount at a low temperature, viz. at commencement of dyeing, in order to minimise surface absorption on the wool, which would on that account give rise to poor rubbing fastness. If it is desired to produce resist effects on the nylon, certain pretreatments may be used for this purpose; e.g. the use of 5 g. Invadine BL (Ciba) and 3 ml. formic acid (80%) per litre, or 5 g. Albatex WSE (Ciba) per litre, for 30 min. at 100°c., followed by hydroextraction and entering into the dyebath.

Generally speaking, the fastness to washing of level-dyeing acid dyes on normal wool is only moderate, and may be considerably less on shrink-resist-treated wool. Dyes of the acid milling type tend to give unlevel results, particularly in the cases where chlorination may have been somewhat uneven. Selected Neolan-type dyes give good solidity on wool and nylon in light and medium shades; and suitable combinations are available for the production of light and medium shades on nylon-spliced half hose. Neolan-type dyes are also extremely useful for producing good tone-in-tone effects on chlorinated and unchlorinated wool,

providing the pH of the operation is carefully controlled within suitable limits.

Selected chrome dyes are, however, particularly suitable for very full shades such as nigger, bottle, maroon, navy, and black, and good solidity on the wool and nylon is obtainable. In this connection it is important to select homogeneous dyes wherever possible, the newly introduced Eriochrome Brown K (Gy) being a good example.

A considerable quantity of wool half hose is made from slubbing-dyed yarns, and a small proportion from dyed yarn. As the faster dyes are used in these instances, little difficulty arises in the ensuing scouring and shrink-resist treatments.

Recently, owing to economic considerations, an increasing proportion of men's half hose has been manufactured from wool mixtures, principally with Fibro, cotton, or nylon. With the cellulosic mixtures, an ingrain effect may be produced by dyeing the wool with chrome dyes, direct cotton dyes then being applied either from the cooling bath or from a fresh liquor. Temperature and pH control are particularly desirable, and the use of organic acids is preferred in order to prevent tendering of the cellulosic component during drying.

In the production of solid shades, the majority of goods are dyed with milling and selected direct cotton dyes; the fastness (especially to washing) of the latter is increased by aftertreatment with formaldehyde, or more recently with products, e.g. Fibrofix or Lyofix, in conjunction with copper salts. Mention should be made here of the copperable direct dyes, e.g. the Cuprofix, Resofix, Coprantine, and Cuprophenyl ranges, which are becoming of particular interest in this connection. The principal shades include navy, brown, grey, fawn, and black; but for the export market the brighter yellows, greens, and blues are in more frequent demand. It must be pointed out that it is important when aftertreating the latter shades to choose a fixing combination which gives the minimum of dulling.

Though cotton and mercerised cotton half hose have not, of recent years, constituted the major portion of the trade, direct cotton dyes are almost universally used. In the case of darker shades, the copperable dyes again find application, in addition to those direct dyes capable of aftertreatment by diazotisation and development.

An interesting recent development has been that of the introduction of all-nylon staple fibre in the manufacture of half hose. Satisfactory dyeing recipes for lighter shades may be based on disperse acetate dyes. Chrome dyes are suitable for heavier shades providing every precaution is taken to ensure satisfactory chroming. This is facilitated by the addition of a reducing agent and formic acid to the chroming bath [29,30]. On the dyeing of wool–nylon and other similar newer fibre mixtures, several papers have recently been contributed, especially by J. G. Grundy [31], G. T. Douglas [32,33], and H. R. Hadfield [34].

### BOYS' AND GIRLS' THREE-QUARTER HOSE

The majority of these goods are made from slub-dyed mixtures. The effect threads usually incorporated in the fancy tops should be dyed fast to washing. Since a large quantity of these goods receive shrink-resist treatment, fastness to chlorination must also be considered.

For those goods of this class which require dyeing after manufacture, acid dyes, chrome dyes, or those of the milling type may be used depending on the shades and degree of fastness required, and similar considerations apply as in the case of the dyeing of half hose.

### CHILDREN'S SOX AND LADIES' ANKLE OR TENNIS SOX

In the case of children's sox, the shades required are relatively few (principally pale blue, pink, lemon, nil green, and fawn), the majority being bleached for white. With the extended use of shrink-resist treatments on wool and wool–rayon mixtures over recent years, there has been a tendency to meet increased demands of washing and perspiration fastness, but with some sacrifice of brilliancy of shade, by the increased use of the acid milling dyes. However, since the successful development in the application of e.g. the Carbolan dyes (ICI), considerable interest has been shown in these for this purpose.

If nylon splicing is present in the heels and toes, owing to the lightness of shade the difficulties of obtaining solidity are less than those arising when dyeing the deeper half hose shades, since dye saturation of the nylon does not generally occur. Children's sox manufactured from cotton–rayon mixtures are usually dyed to pale shades, e.g. pink, sky, etc., by the use of selected direct cotton dyes, preferably on a bleached ground.

Similar considerations to the foregoing apply in the case of lighter shades on ladies' ankle or tennis sox. Since there is also a demand for deeper shades, e.g. saxe, gold, bottle, nigger, light navy, and wine, as in the case of half hose careful dye selection is necessary; for the manufacture of these, 100% wool, 100% cotton, and various mixtures including rayon are most frequently used. Nylon splicings and elasticated tops may also feature.

In the production of very pale shades, particularly for children's sox, the recent introduction of optical bleaching agents has proved advantageous in that, when applied, either in the actual dyebath or as a separate process after dyeing, brilliance of shade is enhanced where the ground colour is good. The degree of bleaching before dyeing may be reduced, and in some cases a sufficiently bright shade is possible without bleaching.

### LADIES' HOSE

This survey excludes the dyeing of ladies' nylon hose. However, even to-day silk, rayon, and mixtures of these together with wool and cellulosic fibres are manufactured in considerable quantities. The dyes employed are, in general, still those that were in use in pre-war years. Long experience has shown that they adequately meet the demands made on them.

On wool hose logwood is still used to a small extent for black, and chrome dyes are mainly used for dark shades. As a large proportion of these wool hose are fashioned, difficulties encountered in achieving penetration of the hard seams may be

minimised by the controlled addition to the dyebath of a suitable penetrating auxiliary of the surface-active type, and by paying special attention to pH and temperature control.

Rayon and cellulosic mixture hose are preferably dyed with direct cotton dyes of similar dyeing characteristics. The increased absorption of many dyes by the more highly dispersed forms of cellulose is well known. Mercerised cotton, for example, frequently dyes to a deeper shade than ordinary cotton, in the same dyebath. Cuprammonium rayon possesses a greater affinity for dyes, and it dyes more quickly, than the other rayons, so that dye migration is best regulated by keeping the electrolyte content of the dyebath at an absolute minimum.

The Icyl (ICI) and Rigan (Ciba) dyes may be employed in conjunction with certain of the older direct cotton dyes for dyeing varying qualities of viscose to the same shade, since they were developed in order to cover the irregular dyeing properties of viscose, associated with this fibre in its early years of development.

When originally introduced many years ago, silk hose were manufactured from dyed yarn, usually grey or black. A historical note may be of interest here—there is a record of Queen Elizabeth being presented with silk hosiery in 1560. More recently, the natural fibre has been thrown in the gum, so that the hose as manufactured require degumming. Much work has been done in an attempt to assess the relative merits of degumming and dyeing separately or in the same bath. No generalisation is really possible, as the results are greatly influenced by processing conditions. However, it is customary, in the dyeing of silk hose with cotton tops, toes, and heels, to employ direct cotton dyes reserving the silk, and neutral-dyeing acid dyes which leave the cotton reasonably unstained. Both types are applied from one dyebath.

### KNITTED FABRICS

With improvements in knitting machinery and the introduction of e.g. the Terrot-type and Interlock machines for tubular knitted fabrics, finer counts of yarn have become more popular for the production of finer-gauge and lightweight fabrics, as indicated in a recent paper by Dutton [35]. Formerly, practically all the trade requirements for fine-wool slumberwear centred round bleached white or shades of peach. For the latter, the Rhodamines have been superseded by the rather less brilliant, but nevertheless faster, neutral-dyeing dyes, e.g. Coomassie Scarlet SE (ICI). Fabrics for the production of ladies' and children's underwear may be dyed to the customary shades of saxe, beige, navy, and grey, using fast acid milling or chrome dyes, preferably the latter when the goods are required to be shrink-resist-treated.

By means of the close regulation possible through pH and temperature control in the dyeing of knitted wool fabrics with the faster neutral-dyeing dyes, difficulties of levelness and penetration have been largely overcome. One important application of these dyes involves the production of fabric for beachwear, where fastness to light, perspiration, and sea-water is required, and selected dyes are used to meet these demands.

Cotton and the rayons have featured for many years in the production of sportswear. In addition to interlock and 1/1 rib fabric, special stitch effects, e.g. eyelet and tuck-stitch structures, are becoming popular. Whilst on rayon the even dyeing Icyl (ICI) and Rigan (Ciba) dyes are desirable, increased demands of light and washing fastness on all-cellulosic materials necessitate the utilisation of direct cotton dyes capable of diazotisation and development in the case of some dark shades, and those suitable for aftercoppering in the majority of other instances. Cellulose acetate fabrics will require dyes appropriate for this purpose.

In the dyeing of large quantities of cellulosic materials, accurate reproducibility of shade is essential, both from batch to batch and within the same lot. Variations are minimised by endeavouring to process batches of approximately similar weights, and also where possible by equalising the lengths of the rolls. Such conditions are, in fact, essential in the highly specialised application of vat dyes [36], where very high processing costs are justified only in cases where maximum fastness to light, washing, and chlorine is stipulated.

Knitted outerwear fabrics are in considerable demand at the present time, and the principal consideration in the selection of suitable combinations of wool dyes is the degree of fastness to the subsequent milling process, i.e. for "cloth finish". In this connection, Barritt and Elsworth's paper on the dyeing properties of chlorinated wool [37] gives details of the production of tone-in-tone and two-colour effects in piece dyeing. Townend [38] has also detailed suitable methods. A new differential wool dyeing technique, applicable to wool and wool-containing mixtures, has been developed by A. J. I. Harding [39] for producing mélange, marl, or tone-in-tone effects, and it is understood that this process is applicable to all forms of knitted hosiery.

### PROCESSING MACHINERY

This survey should not be concluded without some reference to the developments in hosiery dyeing and finishing machinery.

The earliest machines for dyeing hose were similar in principle to the overhead paddle machine, a development of which resulted in the Gorrie or side-paddle type, also still in use. In view of the increased production of finer-gauge knitwear with correspondingly finer structures, the more recent improvements in processing machinery have been made with a view to preserving the delicate nature and elasticity of the materials being processed; this has also been aided by the almost exclusive use of stainless steel for fabrication. Thus for fine-gauge footwear, the Smith Drum type of rotary machine has gained wide interest, particularly in America. In this country notable improvements have been made on the original Gorrie-type machine by e.g. Freeman, Taylor Machines Ltd. in their Gridflow design. Another new principle has been successfully applied in the Samuel Pegg new type hosiery dyeing machine, in which the liquor is circulated through the goods, which undergo the

minimum of movement, thereby assisting in preserving the knitted structure.

In the processing of tubular knitted fabrics, the conventional winch machine has undergone little change in design. The slower-running elliptical winch is preferred for the dyeing of rayon, since e.g. alteration in shade due to differential dye absorption caused by possible mechanical abrasion is minimised.

The use of enclosed winches in the dyeing of rayon fabrics has been discussed in a paper by Ashpole, McFarlane, and Wilcock [40]. This idea has been successfully applied to other types of processing machinery, with considerable savings in steam consumption and labour costs. In the conventional winch-type machine, temperature variations are known to occur in different parts of the dyebath, e.g. between front and rear. In order to obviate this defect, a notable advance has been made by Wolsey Ltd. [41], who have designed a method of heating and circulating by means of an arrangement external to the machine. In addition, automatic devices for controlling dyebath temperatures are being utilised more fully.

* * *

It will be appreciated that in a survey of this nature it is only possible to generalise. Whilst specific dyeing formulæ and fine details of processing have been purposely omitted, the author would like to take this opportunity of thanking all those who have provided up-to-date information in order to make this survey reasonably comprehensive within its limits.

Finally, in stressing the continued need for trained personnel in our industry, it must be anticipated that with the passage of time problems for the specialist will always arise; but it is to be hoped that, when considering their possible solution, innocent advantage is not taken of the would-be wearer, since a recent examination-paper reply suggested that—

". . . a pair of half hose need not be fast to light, if worn by men . . . ."!

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## Discussion

Mr. C. F. WARD: Addition of boric acid may be made to any "neutral-dyeing" dye whose application comes within its pH range, and it does not necessarily rule out the use of any desired neutral auxiliaries. The best proof of its efficacy is to be found in the fact that about 500 tons of wool and wool mixtures have been successfully processed in one dyeworks alone.

Mr. B. KRAMRISCH: Referring to the production of solid shades on nylon-spliced half hose, the author has stated that it is less difficult to obtain solid results in light shades than in medium to full depths. Whilst this statement is true as far as premetallised dyes are concerned, acid levelling and acid milling dyes as a group show preferential dyeing of the nylon in pale shades. This defect, however, can be overcome by addition of an anionic detergent to the dyebath; this acts as a restrainer for the dye on the nylon, thereby resulting in solid shades on the nylon and wool.

Mr. EDWARDS: In practice the use of restrainers is often unnecessary, because a large proportion of these goods are treated for shrink-resistance before dyeing; in most cases, therefore, the wool possesses an increased affinity for the dyes, the resultant shade being more nearly equal on the two fibres.

Mr. H. À BRASSARD: Can one differentiate between "sox" and "socks"?

Mr. EDWARDS: Whilst there is no strict definition of "sox", it is sometimes useful to regard "socks" as synonymous with "half hose" and to retain "sox" for the smaller versions covering children's, ladies', tennis, etc.

Mr. C. P. TATTERSFIELD: Can the author indicate in terms of S.D.C. standards what he considers to be satisfactory standards of fastness for the main categories of hosiery yarns and fabrics?

Mr. EDWARDS: The choice of a suitable fastness test for general application in the testing of hosiery materials depends to a large extent on the nature

of the knitted article, and such factors as e.g. the number of washings likely to be required during the useful life of the garment. Lingerie materials might be expected to withstand repeated washings to the S.D.C. No. 1 test, but a more severe wash, i.e. S.D.C. No. 2, would be considered more appropriate for half hose. Generally speaking, the S.D.C. No. 2 test is now widely used, but occasionally resort is made to S.D.C. No. 3 test for the appropriate fibre.

Apart from wash fastness, perspiration and light fastness are important in certain circumstances, e.g. sportswear, etc., where it may be considered that a fastness to light of 4–5 (*B.S.* 1006) would be satisfactory.

Mr. C. P. Atkinson: It is claimed that the Tensitrol rope- and open-width washing machines (Rodney Hunt) can be used successfully for scouring and washing-off purposes at high speeds (up to 300 yd./min.) virtually without tension. The principle employed is a variable traction of all the drive rollers on the fabric, the amount of variation being determined automatically by the behaviour of the fabric itself as it travels through the machine.

Mr. Edwards: The need for retaining the structural characteristics of knitted materials at all stages during wet processing should be stressed. In this connection, the successful development of the Negafel process was aided by the design of a special roller machine constructed so that tubular-knit fabric was treated under the minimum tension and allowed to balloon out before meeting the nip rollers. In this way, thorough and more even penetration with the chlorinating liquor is readily achieved with the minimum distortion of the fabric.

FRIDAY MORNING, 21st SEPTEMBER 1951

*Chairman* — Mr. E. Isles

# The Rise and Development of the Wool Dyes
## A Brief Historical Survey

J. Baddiley

(Presented by A. H. Knight)

The modern wool dyes owe nothing to Nature. They arose from attempts to make the sparingly soluble basic dyes of the pioneer period of dye synthesis more suitable for application from aqueous solution. The sulphonic acid group provided the clue to the development of the acid wool dyes. Sulphonation also opened the road to the discovery of the rich field of azo dye intermediates, which have been the source and inspiration of an immense range of cheap and versatile acid dyes for wool, supplemented by the brighter triphenylmethane acid dyes on the one hand, and the faster (to light) acid anthraquinone dyes on the other. Fastness to wet treatment and light was achieved by the discovery of dyes suitable for metallic complex formation. Acid dyes of this type ended the dependence of the wool dyer on natural colouring matters. Modern trends aim to avoid the fibre damage associated with the chrome dyes, either by improvement of the latter or by a departure from the idea of complex formation. New structural features have been introduced which promote fastness to wet treatment in ordinary acid dyes.

It is to the chromophoric group that the writer on dye chemistry inevitably turns when seeking a basis of classification for his material. To many chemists it would appear difficult, if not actually misleading, to attempt any sort of general treatment within the confines of a classification based entirely on methods of application. This Conference has, however, been organised for the purpose of surveying progress in the colouring of textiles, and it is only right that if dyeing materials, e.g. dyes, are to be included, they must fall into line with the general plan of the discussions.

As a matter of fact, the present treatment might prove to have, at any rate, one good point, in that it tends to place emphasis on those structural features of the dye molecule upon which its utility and mode of application depend, the great technical significance of which is liable to escape the reader of the ordinary type of text-book of colour chemistry unless he is well versed in the technique of dye application and, indeed, in the wet treatment of textiles in general.

It is not a bad thing, then, for the dye chemist to be pushed into reviewing his material, and studying its evolution, from the point of view of the man who uses it, and in doing this there is no call for him to be condescending to the tinctorial arts. The give and take between the two technologies is mutual and equal. No ancient craft has been quicker to advance its technique through the application of scientific knowledge and method than has the "wet" side of the textile industry. It has been inspired in this largely— perhaps mainly— by the development of the dye industry, which always runs hot-foot on the heels of advancing science, and is unique in the way in which it has made industrial research one of the major functions of management. The enormous initiative of the dye industry, however, has always been powerfully influenced, and at certain stages prompted, by an appreciation of the user's problems. Great discoveries may come to it by accident or from flashes of genius, but, however great the chemical skill available, such discoveries would fail to be properly exploited without deep insight into the needs and scope of textile technology. Accidental discoveries do occur, and are well advertised because of some romantic appeal they have to the imagination of men, but it is noticeable that they occur most often in quarters which have been well prepared for their reception in the manner indicated. The great majority of dye inventions are, however, contrived by careful planning and team-work, and by definition of research targets in terms of the user's aims in regard to the quality and economy of his own production.

This picture of orderly progress by scientific method did not always characterise our industry, and in its early days there was one period when it was a hectic adventure, and another of ruthless war on the older, natural dyeing materials. Since the industry of making artificial dyes is now approaching its centenary, it would appear interesting to review the progress of the wool dyes over the whole period, dividing it roughly into decades and characterising each by some outstanding event which might be held to have had a dominating influence at the time. This plan seemed to work until about mid-way, say the end of the first decade of the twentieth century, when the pattern of future development appeared to have become fixed. This, however, is getting too near the time of personal and current activities for one to be sure of one's perspective. So let us go back to the beginning, and do our generalising where there is a little more elbow-room.

### THE 1860s— MAGENTA DAYS

The products of the first great wave of invention which launched the dye industry were basic dyes. There was no volition in this: it just happened that the early discoveries were all made from aniline (impure) by "cooking" it in various ways. The processes were primarily oxidative, but this was not known at the time, nor indeed was any other aspect of the underlying chemistry of the magenta dyes.

Perkin's Mauve came first (1856), but had only a very short life, not because of any lack of fastness, but because it was very expensive, even for those days. Magenta followed quickly (1859), and became the keystone of the industry for a decade. Magenta, the product of "cookery", was in its turn cooked up with various reagents and gave a family of derivative dyes, such as Hofmann's Violet, Iodine Green, and Aniline Blue. A remarkable range was achieved

in a few years. No thought was given to their suitability for any particular section of the textile trade. They varied in basicity, and were sold as "water-soluble" or "spirit-soluble" as the case might be. They sold themselves on their brightness and wonderful beauty.

There was a scramble for patents and some litigation; manufacturing costs ran high, but profits soared. There were in England at that time, however, men who tried to get an understanding of the chemistry of the new dyes and to rationalise their manufacture. Hofmann and Nicholson were the first to have an inkling that something other than (pure) aniline was involved in the formation of Magenta, and under the influence of these two men a more scientific outlook began to creep into the industry. When Hofmann's Violet was seen to be the result of the alkylation of free amino groups in the parent Magenta, it was not a far step to the alkylation of aniline itself. From dimethylaniline Methyl Violet was then prepared, and quickly replaced Hofmann's Violet, as this dye had in its day displaced Mauve, on grounds of cost.

The alkylanilines (dimethyl-, diethyl-, and ethylbenzyl-aniline) helped the expansion of the range. They also helped to make the invention of dyes more systematic, so that by the end of the 60s the happy-go-lucky methods of the early days were giving way to the conscious synthesis of new dyes. This decade is being passed over very sketchily because it did not do the wool dyer much good, though no doubt he allowed his scruples to be overcome at times by the great beauty of the "aniline" dyes. But the period has its interest for us because an event occurred which had far-reaching importance in dye technology, besides pointing the way to the discovery of real wool dyes.

Nicholson had turned his attention to Aniline Blue, the fully phenylated rosaniline, made by condensing Magenta with aniline. Blue is a master colour, ranking only with black in the commercial hierarchy of dyes; but this blue, which was spirit-soluble and could appeal only to the silk dyer, was a challenge to Nicholson's technical instincts. In an attempt to make it water-soluble and give it wider application, he treated it with sulphuric acid. His experiment resulted in the introduction of sulphonic acid groups, and this was the start of sulphonation as a technique in the manufacture of artificial dyes.

Nicholson's Blue, the sulphonic acid of Aniline Blue, can hardly be regarded as an acid dye in the proper sense (it was sold for wool dyeing as Alkali Blue), but it was a signpost pointing the way. The sulphonation reaction came to full fruition at a much later period, when the remarkable development of naphthalene and benzene derivatives set in for the supply of azo dye intermediates. It figured prominently in the next decade, when it facilitated the development of a commercial synthesis of Alizarin. It was also used for the sulphonation of Alizarin itself, and of various basic dyes, in order to make them available to the wool dyer. All this came later, but it spotlights Nicholson's discovery as the feature of the Magenta decade which had the greatest significance from the point of view of the evolution of the wool dyes.

### THE 1870s— THE AGE OF ALIZARIN

The successful establishment of an economic process for the manufacture of Alizarin was the outstanding feature of the '70s. Its influence extended far beyond this period, of course, for it was the first conquest of Nature on the grand scale by industrial chemistry. It made the cultivation of madder unprofitable and brought it to an end. It also brought the flourishing British dye industry to an end.

As Alizarin does not concern us immediately in connection with the wool dyes we may dismiss it briefly. Caro in Ludwigshafen and Perkin in England simultaneously hit upon feasible manufacturing methods based on the published work of Graebe and Liebermann. The following table tells the remainder of the story—

Production of Alizarin (tons) by B.A.S.F.* and by Perkin & Sons

| | B.A.S.F. | Perkins' |
|---|---|---|
| 1869 ... ... | — | 1 |
| 1870 ... ... | — | 40 |
| 1871 ... ... | 150 | 220 |
| 1872 ... ... | 500 | 300 |
| 1873 ... ... | 1000 | 435 |

In face of this competition Perkin sold his works and retired.

Caro and his associates were not content with replicating the natural dye, of course, and they soon began to expand anthraquinone chemistry around the new Alizarin technique. New mordant dyes soon began to appear. It was not that, however, which made Alizarin such a portent, for after all it is, as a dye, now almost dead. It came at a time when dyemaking was in a stage of transition. It was the first premeditated synthesis of a dye. All that had gone before it was the result of an empiricism verging on cookery-book methods. From now on the dye industry was to be developed by systematic research, and to be inspired by the rapid progress which organic chemistry was now making, as instanced by the work of Hofmann and the two Fischers on Magenta, by the rapid expansion of knowledge of the reactions and isomerism of aromatic compounds following Kekulé's explanation of the structure of benzene, and by the beginning of Baeyer's classic work on Indigo.

Caro's success with Alizarin gave him confidence and power to take full advantage of these changes. He was a great innovator and has a dozen or more of the classical dye inventions to his credit. He had a keen perception of industrial possibilities and led his firm into new enterprises. It is not surprising, therefore, that Caro's name is linked with the early beginnings of the acid wool dyes.

The campaign was actually opened by Roussin's discovery of his famous Oranges I, II, III, and IV, between 1876 and 1878. Orange II, which enjoys some reputation 75 years after its discovery, is the ancestor of all the azo acid wool dyes. It was not, of course, the first azo dye. Witt's Chrysoidine (1875) was the first dye to be manufactured by diazotisation and coupling by Griess's method. It

* Badische Anilin- und Soda-Fabrik

is not a very valuable dye, but it opened Caro's eyes to the possibilities of Griess's discovery of the diazo compounds 18 years earlier. His famous Fast Red, patented in 1878, was the answer.

Prior to Caro's Fast Red there had been a general impression that the azo compounds must all be yellowish or brown. Roussin's Orange seemed to confirm this. Orange II is made from diazotised sulphanilic acid and $\beta$-naphthol. Caro went into the naphthalene series for his first component and Fast Red opened the flood-gates for the rush of azo dye invention which quickly followed. Caro obtained a patent for his Fast Red, around which B.A.S.F. fought and won many legal battles. Roussin's Oranges were not patented, being within the ground covered by Griess's published work on the coupling of diazo compounds as far back as 1864. They put the dyer in possession of a "new technical effect", however. Caro was luckier, and, since his naphthylaminesulphonic acid diazo component was outside the scope of Griess's results, he obtained a valid patent.

About the time that Roussin's Orange was attracting so much attention, acid dyes began to arrive from another source, namely the sulphonation of spirit-soluble and basic dyes. Acid Yellow was made by this method from aminoazobenzene, Acid Magenta from Magenta, and Light Green SF from the triphenylmethane dye derived from benzaldehyde and ethylbenzylaniline.

By the end of the '70s the acid wool dyes had definitely arrived, and, though the range was still restricted, the threat to the natural red wool dyes (Cochineal) at least could be detected. There seemed, however, to be no danger in the much more important blue-to-black field, except that contained in the slow unfolding of the way to synthetic Indigo, on the chemistry of which Baeyer had now commenced his classic work.

### THE 1880s— THE ADVENT OF THE AZO DYES

This decade has been named after the azo dyes because it was during the '80s that their development gave a clear indication of the important rôle that they were destined to play in the future expansion of dye technology. They owe this position to several causes, the most important of which is the enormous répertoire of intermediates which can be drawn upon for their synthesis. This arises from the unique capacity of benzene and naphthalene to add on by substitution a variety of groups which can influence the optical, dyeing, and fastness properties of the derived dyes. These possibilities are multiplied by position isomerism; for example, the number of aminonaphtholsulphonic acids which are theoretically possible runs into hundreds, out of which a mere handful have so far been employed in manufacture. A further reason is the prominent part that sulphonation has played in this blossoming of benzene and naphthalene chemistry. It is, therefore, easy to make a very great variety of intermediates capable of being used either as diazo components or as coupling components in the synthesis of azo dyes, and at the same time to ensure the presence of sulphonic acid (sulpho) groups in the finished products.

It was hardly to be expected that the enormous potentiality of the azo dyes was immediately seen in the '70s, when Roussin's Orange and Caro's Fast Red first appeared. Caro himself, fresh from his victory over madder, was more impressed by the fact that his Fast Red competed with the mixture of cochineal and fustic with which the dyers had produced their dark reds. The "novel technical effect" involved in the application of dyes from a simple acid bath came home to Caro later, however, and he realised that there was only one way to grapple with the problem, and that was through the intermediates by a mass research attack. The German dyemakers were all of the same mind apparently, and in the '80s there was such a development of azo acid dyes that by the end of the decade the war of artificial *versus* natural dyes was being carried right up to the enemy's threshold.

This did not happen all at once, and in retrospect the progress of the azo acid wool dyes during this period appears slow. The acid dye idea had taken firm hold, however, because there was progress in this type in other fields besides the azo one. Moreover, it was in the mid-'80s that cotton was put into a parallel position by the discovery that a certain type of azo dye was substantive to this fibre (Congo Red 1884, Benzopurpurin 1885). By the end of the decade azo chemistry had advanced up to the frontier of blacks for both wool and cotton, which could be applied in a simple one-bath process, without mordants or other complications. From then on the development of the azo dyes blazed like a bonfire, which is burning as brightly as ever. To complete the analogy it may be said that Roussin's Orange and Caro's Fast Red were the sparks which ignited it; Congo Red and Benzopurpurin fanned the flames.

The first additions to the acid wool dyes in the early '80s ranged through orange and ponceaux to bordeaux. They were obtained from sulphonation products of $\beta$-naphthol. These were disulphonic acids, and when separated were designated *R acid* (the 2:3:6-isomer) and *G acid* (the 2:6:8-isomer) according to their reddening or yellowing tendency on azo combinations made from them. The separation and study of these acids first drew attention to the effect of isomerism on the properties of a dye. The monosulphonic acids of naphthol were next prepared and isolated. The 2:8-isomer was called *Crocein acid* after the Croceins and Crocein Scarlets made from it. According to Caro the latter replaced his Acid Magenta. 1:4-Naphtholsulphonic acid was prepared from $\alpha$-naphthol, but afterwards in purer form from naphthionic acid. It gave brilliant reds including Azorubine (Carmoisine).

These were the early beginnings of the complex technology of the naphthalene intermediates. Unfortunately it is impossible to follow the further development of this fascinating subject in a short review confined to wool dyes.

Besides the new azo dyes, discoveries of new acid dyes for wool were made in the other classes, particularly in the triphenylmethane series. By 1880 the problem of the constitution of the Magenta dyes had been cleared up by the classic

work of E. and O. Fischer, and soon new synthetic methods began to be discovered. One of these, the phosgene method of introducing the central carbon atom, resulted in Acid Violet 4BN (1883). Another, the formaldehyde method, gave Formyl Violet and Wool Green S (1883). A new intermediate, *m*-nitrobenzaldehyde, led to the discovery of the Patent Blues (1888). When we add Tartrazine (1884) (the first dye containing a pyrazolone component) to this list of leading dye discoveries of the period, it will be seen that the acid dyes now covered quite a wide range of shades. In the last year of the decade the first black appeared, the azo dye Naphthylamine Black D, a very purplish sort of black, but a valuable dye and a portent of great developments to come.

### THE 1890s— INDIGO PURE

Without any doubt the most impressive event of the closing decade of the nineteenth century was the commercial production of synthetic Indigo— *Indigo rein* (*pure*) was the name under which the B.A.S.F. put it on the market. The replacement of Indigo cultivation by industrial synthesis was not only something for the students of economics to wonder at, it was a technical achievement of the highest order. When one sees how quickly some of the things have come about which have had a revolutionary effect on dye technology, it is rather a shock to realise the long intervals in the chain of events leading to Indigo pure.

Baeyer started his work on Indigo as early as 1868, and it was not until 1883 that he was able to publish the structural formula with which we are now familiar. Various syntheses were published by Baeyer and others between 1880 and 1890, but it was not until later in the '90s that a manufacturing process was established which was capable of displacing the natural product.

The story of this masterpiece of industrial enterprise and its economic repercussions are well known and need not be recounted. More intriguing, from the point of view of wool dyeing, is the fact that already in the '90s the range of acid dyes was rapidly extending into the blue and black fields, so that when Indigo pure began to replace the natural product its decline as a wool dye was already assured.

Logwood (the third member of the great trio— Indigo, Madder, and Logwood) was included in this menace, too, and the flag went up, so to speak, with the discovery of Naphthol Blue Black in 1891. This dye, along with Naphthylamine Black D, became the source of the standard blue–black and black mixtures for acid dyeing, and has held its position ever since. Its manufacture centres around three mass-produced intermediates, and its selling price of a few pence per pound before the first world war was as much a technical triumph as synthetic alizarin or indigo.

Another important wool dye appeared in 1892, Sulphon Cyanine, which, as compensation for the fact that it would not dye in an ordinary acid bath, showed an improvement in wet-fastness over the level-dyeing types. In certain trades it competed strongly with indigo.

Only the highlights can be dealt with in a brief review of this type, and so it must be taken for granted that discoveries of a decisive nature, like Naphthol Blue Black and Sulphon Cyanine, were followed by analogous developments. The latter, for example, led on to Sulphon Cyanine Black and the Nerols, with similar dyeing and fastness properties, and may indeed be considered as the parent of the milling fast class of substantive wool dyes which came into prominence many years later. The main point is that during the '90s the wool dyes of the azo class gave ample proof of their enormous potentiality.

As far as acid wool dyes were concerned, there was no lack of development in groups other than the azo. The bright but fugitive triphenylmethanes received a boost from the discovery of Erioglaucine, Naphthalene Green, and the Xylene Blues. The most important event in this direction, however, took place in the anthraquinone series, hitherto the source of nothing but mordant dyes which mainly interested the cotton dyer and printer. The discovery of a new race of anthraquinone acid dyes was the work of R. E. Schmidt, and they appeared on the market during the '90s in a regular procession under romantic names like Alizarin Cyclamine, Emeraldol, and Sapphirol, to say nothing of Alizarin Blue Black and Cyanine Green. Thus, by the end of the decade, the acid wool dye range covered every requirement in regard to level dyeing and light fastness. Wet-fastness was the only serious problem in this field.

Where a high degree of fastness to wet-treatment was essential dyewoods or the premordant dyes of the Alizarin class had to be used. The range of the latter was greatly improved during the '90s by the brilliant work of Bohn, whose novel method of preparing polyhydroxyanthraquinones resulted in the Anthracene Blues. Certain modifications of the process left residual sulphonic acid groups in the molecule, in which case the resulting dyes (distinguished from the other Anthracene Blues as S brands) were water-soluble, and could be applied from an acid dyebath and then afterchromed.

The azo chemist was quick to seize on the idea of acid dyes which would exhaust in a normal bath, into which the chrome could then be entered in order to fix the dye— a two-stage process, but less troublesome than the older mordant dye and dyewood techniques. It might be thought that Diamond Black F, discovered as early as 1889, would have pointed the way, but it owes its mordanting properties to a salicylic acid residue, and salicylic acid dyes in the azo series had been studied often enough, but had found their outlet mainly in calico printing. Another type of early azo chrome dye was represented by the Chromotropes discovered in 1890, and a still earlier one was Carmoisine (1883), but these offered no reliable lead, and real progress did not come until the recognition of the virtues of the *o*-aminophenols. This came later, but the close of the decade (and century) witnessed the appearance of one of the classic azo chrome blacks, Acid Alizarin Black SE, which may be regarded as the precursor of the series of azo acid chrome dyes.

### THE 20TH CENTURY— THE SEARCH FOR FASTNESS

The course of dye development in the twentieth century has been too disturbed by wars and economic upheavals to lend itself to treatment in decades. Nevertheless, there was at first a period— up to the outbreak of war in 1914— which was distinguished by intense activity in the anthraquinone field. René Bohn's discovery of the first anthraquinone vat dyes in 1901 started it off, and it continued for well over a decade. The work was so fruitful in invention that the new vat dyes still presented all the aspects of novelty and innovation when the outbreak of war put an end to speculative research work. The bulk of the work on which the anthraquinone vat dye range is founded had, however, been done by this time, having engaged the energies of hundreds of chemists. The period up to 1914 could, therefore, with some justification be labelled the *anthraquinone age* in order to distinguish it from the earlier sections of this review.

This mighty effort was almost entirely for the benefit of cotton. The evolution of the wool dyes had already had *its* period of high fever of excitement in the days of the pioneer azo acid dyes, and the colossal development of the intermediates field which followed it, especially in the chemistry of naphthalene. The aftermath of this was still to be reaped, and we find that the development of the wool dyes was by no means at a standstill in the early 1900s. As in the case of cotton, the trend was in the direction of increased fastness.

The advent of the anthraquinone vat dyes was revolutionary. They created entirely new standards of fastness, which enabled cotton to be used in ways previously undreamed of. This advance was so great that it was welcomed even at the cost of a very considerable complication in application technique. In the case of wool the position was quite different; the problem was to develop fastness standards up to the level of the reputation already enjoyed by the older natural dyes. A considerable victory had been won in the past by the acid wool dyes as a result of the enormous simplification in dyeing technique which they had made possible. It was necessary to preserve this economic advantage while improving fastness standards.

The developments of the '90s had resulted in steady progress in dyes in both the azo and anthraquinone classes of wool dyes, which showed a general all-round improvement. Lack of wet-fastness was, however, still a weakness, though there had been a definite indication of the direction from which a drastic improvement in this respect was coming, and that without overmuch sacrifice in ease of application, viz. the afterchrome dyes. This promise was quickly fulfilled in the all-important field of blacks, for Diamond Black PV was discovered in 1902 by Kahn, and the Eriochrome Blacks by Hagenbach two years later. By the time the artificial dye industry celebrated its jubilee in 1906, the last defences of the natural colouring matters were down, and the chemist could now concentrate his attention on the perfection of what were now the permanently established lines of wool dyes.

In the case of the chrome dyes, apart from amplifying the range, the principal objective was to simplify the application of these dyes as much as possible. This led to the invention of the metachrome or one-bath process, a technique which is applicable to selected dyes made from diazotised *o*-aminophenols and suitable coupling components. A range of dyes gradually emerged which possessed the right combination of properties to enable the acid dye to go on to the wool and form its chromium complex without precipitation or unevenness. A number of derivatives of *o*-aminophenol were prepared, and the enormous répertoire of azo coupling components was thoroughly explored; nevertheless, there is still a steady trickle of patents year by year covering dyes suited to this technique, so important has it become in the fast dyeing of wool.

It is a curious fact that the first azo dyes, consciously prepared, were made by Peter Griess from diazophenols. He took out a patent in 1877 which never came to anything, naturally, because of the great sensitiveness of such dyes to acid and alkali. When, however, their value as chrome dyes was discovered more than 20 years later, Griess's publication proved a serious obstacle to the patenting of dyes of this type. A similar difficulty arising from Griess's publications prevented Roussin from getting the benefit of patent protection for the pioneer acid wool dye, Orange II. The early metachrome dyes were given a measure of protection by user patent, but this was not possible in Roussin's case.

It must be pretty obvious that, in developing a series of chrome dyes suitable for one-bath dyeing, many compromises have to be made between properties which one is trying to accentuate and properties which are undesirable. That is the reason why there is still scope for new invention in this series even after 50 years of steady work.

Another difficulty is that the mordanting process is accompanied by a considerable deepening of shade. The range of chrome dyes has, therefore, been hardest to fill out at the lighter end. There is plenty of scope, however, in all shades, witness the reception accorded to Metachrome Brilliant Blue, introduced just before the second world war. In the chrome wool dyes we have, then, a development which dates essentially from the beginning of the century and is still a fertile field for invention.

In the meanwhile there have been odd patches of discovery in the ordinary, level dyeing, type of acid wool dye. Work in the prolific azo field will never stop, but there have in modern times been few major discoveries of wool dyes of the level dyeing type in this group, except in the acid yellows, where there has been a steady pressure in the direction of light fastness and greenness of shade. This has resulted in an exhaustive study of pyrazolone chemistry, heterocyclic compounds like the pyrazolones being hypsochromic in comparison with coupling components of the benzene and naphthalene series. The Xylene Light Yellows (ca. 1908) were the outcome of this work, but it has continued up to modern times. It has its origin in Tartrazine, discovered as long ago as 1884, but it

was almost a quarter of a century before the pyrazolones began to be systematically exploited. They are used as "yellow" components in every class of azo dye to-day, e.g. in the chrome class, where they furnish reds, owing to the bathochromic effect of the addition of chromium. They are the main source of yellows in the level dyeing and "milling" types of acid dyes.

No other new class of azo coupling component has been found which has merited systematic exploration like that to which the pyrazolones have been submitted. On the other hand, the original well of benzene and naphthalene derivatives has by no means been pumped dry. It is rather a surprise to note that a dye like Azo Geranine was not discovered until as late as 1902, but inventors have rather turned away from the level dyeing type of azo acid dyes in search of a milling fast type.

There had been earlier intimations of such a possibility, e.g. the Sulphon Cyanines, which showed an advance in wet-fastness over the ordinary acid dyeing type, at the expense of the need for a "neutral" dyebath. The real urge, however, came from the chrome dyes, the very success of which created entirely fresh research targets, as is inevitably the case in the dye industry. The high degree of fastness attained by forming the chromium complex is accompanied by a deterioration in the fine quality of the wool. It was discovered that this can be avoided by the use of acid dyes of a new type which has been developed extensively in the period between the wars. By their use a degree of wet-fastness is attained which falls short of the high standard set by the chrome colours, but is sufficient for a large section of the trade. As usual their development has been accomplished by striking a compromise between a high standard of fastness and good dyeing properties, i.e. approximating as nearly as possible to the ideal condition of acid dyeing; the two trends are sometimes opposed to each other.

The wet-fastness of these dyes is dependent on extra affinity for the fibre conferred by configurational features of which there are several different types. The factor which gives dyes derived from benzidine their affinity for cotton also confers on them an affinity for wool which is greater than that which would normally be expected from them as sulphonated azo compounds. A few direct cotton dyes can be dyed on wool, but generally with indifferent results on account of failure to level. Now if benzidine is substituted in the 2:2′-positions, as in *m*-tolidine, the affinity for cotton of dyes derived from it is lowered, but the latter are generally quite reasonable wool dyes. *m*-Tolidine is, therefore, used as a source of milling fast acid dyes such as some of the Polar Reds and Oranges.

The colloidal properties of the direct cotton dyes gave another clue. In an attempt to exploit the tendency of soluble derivatives of long aliphatic chains to micelle formation, such chains were introduced into dye molecules which would normally be expected to behave as acid dyes. The idea worked in both the azo and acid anthraquinone series, and gave rise to the Carbolan (ICI) series. In the anthraquinone series of acid dyes the doubling of the molecule around a central methylene group has been successful in generating milling fast types, e.g. Alizarin Supra Sky SE and Brilliant Alizarin Milling Blue G. This constitutional change is just the sort of thing which would work in the direction of cotton affinity (cf. Benzo Fast Scarlet 4BS), and emphasises the relationship between the factors which make for substantivity in cotton dyes and for milling fastness in acid wool dyes.

Another new class of wool dyes which came into prominence between the wars and is still developing is the premetallised type, which may be explained as an attempt on the part of the dyemaker to relieve the dyer of the trouble of converting chrome dyes into the metal complex state during the dyeing operation. Conditions were discovered under which suitable azo dyes derived from diazotised *o*-aminophenols would react with chromium salts to form products which could be isolated and sold for use as acid dyes. The first extensive range of dyes of this type were the Neolans (Ciba). They stand in the highest class of wool dyes for all-round fastness but have the serious drawback of requiring a very strongly acid bath for their application. Prolonged heating under such conditions has a deleterious effect on wool.

Summing up, the main trends in wool dye development between the wars have been towards increasing fastness (wet-fastness particularly) along three main lines— (1) increasing the range of the chrome dyes, especially the one-bath type; (2) widening the range, and if possible ameliorating the dyeing conditions, of the premetallised type; (3) discovering constitutional factors which will confer milling fastness on otherwise normal acid-dyeing types. As far as can be judged from the patent literature, post-war activities have been mainly in the same direction, the azo group taking the lion's share. The azo and anthraquinone chromophores have monopolised the field in recent years as far as wool dyes are concerned. For sheer brilliance, however, the acid triphenylmethane dyes can never be left out of account, and, although the appearance of a new member of this series like Brilliant Indocyanine 6B (1926) is a rare event, it is a reminder that the chromophore into which Nicholson first introduced a sulphonic acid group still has possibilities for the inventor of wool dyes.

## Introductory Remarks to the Discussion*

In my written communication I have endeavoured to give an outline of the history of the synthetic dyes which are, or have been, used in the dyeing of wool.

I have not the slightest doubt that, in attempting to review such a wide subject in so small a space, I have, in the interest of brevity, been tempted into generalisations with which there may not be common agreement. If there are any glaring examples of this in my script, I am sure they will not get past an audience consisting of members of the Society of Dyers and Colourists. I shall therefore make my own comments as short as possible, for to tell the truth I am anxious to hear yours, before I commit myself more deeply on matters on which there may be more than one opinion.

In the opening paragraph of my paper I have put some emphasis on the mutual dependence of dye-maker and dye-user in the development of their respective technologies. It occurred to me while writing this how wise the University of Leeds was when, in A. G. Green's time, it instituted a degree course in Colour Chemistry and Dyeing, a four-year course involving the simultaneous study of basic science and the technology of two separate but integrated branches of industry, each of which has reached a high pitch of rational development. I hold the view that such a discipline could be a valuable education for anyone, apart altogether from its value as a training for a specific career. I think it encourages initiative and ambition when a man learns his science and its application simultaneously. Even the empirical aspects of the technology he is being taught have importance in shaping his mind, besides merely adding to his knowledge. In the words of Dr. C. J. T. Cronshaw, speaking at the Society's last annual dinner[1], "you must, so to speak, let the dog see the rabbit".

But how profoundly I differ from the remainder of the paragraph in Dr. Cronshaw's speech from which I have just quoted the concluding sentence. He is reported as saying " . . . the only method of training technologists is to train scientists and then let them be engaged within industry . . . . they cannot be deliberately and formally trained as such in any other place". Surely it is no function of industry to give "formal training". It is experience that a man must gather from industry, which he will do most profitably and with the least friction if he has previously acquired some knowledge of the principles and practice of that industry in a good school of technology such as one finds in certain well known American, German, and Swiss institutes, and in the technological faculties of certain of our own universities.

There are very few firms with such large organisations that they can arrange training schemes for pure science graduates in order to give them a grounding in the technology of their trade. In the ordinary firm acute misunderstandings can arise between a young scientist, fresh from the university and perhaps a bit above himself, especially if he has been for a year or two in a famous research school, and the old hands in industry who know everything about the job except the knack of directing the energy of over-confident young scientists into profitable lines of work. If, on the other hand, our young recruit arrives with some measure of technical background to his science, he has a much better chance of putting himself over.

If I did not believe this I would go all the way with Dr. Cronshaw, or even further, and say (I am quoting him again) "There is within industry a potent directive force towards novel things which can only be experienced by dint of having our work and being within an industry". If one follows this remark to its logical conclusion the budding technologist would be placed in industry directly from school, to learn as he earns, and to acquire the science necessary for the completion of his training by part time and private study. As a matter of fact many of the finest technologists of my day have been trained in this, the "hard" way, others by the method I advocate (technological faculties of universities or of university standing), and others again by Dr. Cronshaw's method. His method—to confine formal training to science alone—is the most hazardous, I consider, and when it does succeed (outside big business, of course, where the trainee tends to be feather-bedded) it may produce a very good type of man. You never catch Dr. Cronshaw entirely in the wrong, but his remarks were perhaps a bit unfortunate at a time when a desperate eleventh-hour effort is being made on behalf of higher technological education in this country.

I have said something in the introductory part of the printed paper on research targets and planning. I would like to mention here how much the dyestuff chemist hopes to gain from the studies of the dyeing process, and of the behaviour of dyes in the dyebath and on the fibre, which are now being made with the aid of thermodynamics and the experimental technique of modern physical chemistry. The precision and understanding which this work is bringing to bear on the subject should be helpful to those whose aim is to synthesise new dyes to fulfil functions on which there has been only empirical information in the past. I should like, on behalf of dyestuff chemists, to express my appreciation of the encouragement the Society has given to such work by its publications in the *Journal*, and to Dr. Vickerstaff for his very able survey of the field in his recent book[2].

On top of all this, the organisation of Conferences like the present one, in which the difficulties of the industry and the deficiencies of its raw materials are brought out, should help enormously in developing the technological outlook of the man whose initiative is, in the long run, the cause of all new dye discoveries, the man at the laboratory bench, an organic chemist in every instinct and a technologist by training and experience.

* These remarks were written by Mr. Baddiley and read in his absence by Mr. Knight. They contain Mr. Baddiley's views on matters of general concern to members of the Society, and the importance of recording them in full has been increased by his death shortly after the Conference—*Editor*.

Going back to early history, to the Magenta days, and the pioneer period which reached its climax with the synthesis of Alizarin, there must be some very interesting human stories associated with the fortunes made and fortunes missed in those days. Perkin's behaviour in selling his business has aroused much speculation and controversy. Nicholson's action in retiring early, and abandoning his child to his less competent business partners, is even more puzzling. These same business men later failed to capitalise the great industrial property which could have been built around A. G. Green's discoveries in the Primuline field. Caro, who founded the German industry, always paid the highest tributes to the British pioneers, but he must privately have regarded England as the home of brilliant failures.

All sorts of excuses have been made for this "tragedy"— alcohol duties, patent laws, etc. A more reasoned explanation is offered by Professor Kruyt in his Jubilee Memorial Lecture to the Society of Chemical Industry[3]. In the course of a brilliant study of the relationship between pure and applied science, Professor Kruyt illustrates the dependence of the one on the other by Perkin's failure to carry on his business successfully, which, he argues, was due to there being in England at that time an insufficient background of pure science to ensure the stability of an industry so dependent on scientific initiative. In Germany, he says, conditions were the reverse of this; therefore, the industry flourished *there* while it languished in England. I think the Professor has chosen an unfortunate example for his thesis, with which otherwise I am in general agreement.

Actually, the best organic chemical research and teaching school in the world at that time was Hofmann's laboratory in London. Here worked and studied men like Perkin, Nicholson, Griess, Martius, Abel, and many others. Hofmann's ruling passion was the chemistry of aniline and its derivatives. Perkin complained that he could not get research workers capable of taking some of the burden off his own shoulders. I suspect that Perkin was an ultra-individualist and *liked* to run his works single-handed. When he came to the point where he had to plough profits back into the business by building up a research team and improving his plant in order to compete with Caro, he decided to shake himself clear of business worries while his fortune was still intact. As for the scientific conditions in Germany at that time, I cannot do better than quote Caro—

> . . . no more than isolated rays of light were coming from the laboratories of Liebig, Wöhler, Kolbe, and Bunsen. Liebig's burning indictment "On the Condition of Chemistry in Prussia" had not been taken to heart, the great Universities of Bonn and Berlin still awaited their awakening. Hofmann in England was the intellectual leader of that country's chemical industry . .

It is worth recalling, too, that Caro himself was once within reach; he worked as a chemist in a Lancashire print works and actually took out his first patent with Dale in Manchester. Back in Germany, Caro realised that a dyestuff industry could only be built up and made competition-proof in one way. He discovered the technique of industrial research and made it a factor in management. As an example of Caro's outlook he told his works chemists (plant managers) that they needed to keep up their reading of chemistry even more than the research workers, because on account of the nature of their responsibilities they were in greater danger of slipping out of scientific habits of mind and approach to their problems. If you ask me why England lost her early dyestuff industry, my answer would be, simply— Caro.

Under the influence of men like Emil Fischer and Adolf von Baeyer, great schools of organic chemistry grew up in Germany, from which the early research teams could be recruited. These leaders *themselves* did research work on problems of dyestuff chemistry. It stirred me when Sir Robert Robinson, in a recent broadcast to illustrate the methods by which the organic chemist determines the constitution of a product and confirms his deductions by synthesis, took as his example the Baeyers' classic work on indigo.

I would have liked to have given you a more adequate picture of one of the dyestuff industry's greatest achievements, the development of the naphthalene intermediates. You can get a glimpse of it if you will refer to the new edition of *Chambers's Encyclopædia*, where I have given a highly condensed account, chiefly in the form of charts. Another side of the picture is to be seen in the collection of specimens from the classic work of Armstrong and Wynne, now housed in the Blackley laboratories of I.C.I.

I have dealt with the latest phases in the development of the wool dyes in outline only, merely illustrating the trends. My excuse for this is that a good and detailed account was given to the Society in 1949 by Mr. A. H. Knight, to whose paper in the *Journal* I would refer you [4].

## The Future

After reviewing the past and taking careful stock of the present, there is a natural temptation to try to see into the future. One would like to be able to discuss the first glimmering of a new discovery heralding a complete departure from well worn paths of development. The last great discovery in the dyestuff industry disclosed a new chromophore, that of the phthalocyanines. This is still a matter of recent history, and nothing comparable can be expected for a generation at least. But even if phthalocyanine were to prove the last and final epochmaking invention of the industry, dyestuff chemistry must not be thought of as in any sense played out. In the azo field, particularly, new patents pour out regularly, and rarely does a week pass without some development being recorded which presents some degree of novelty. That this is possible after eighty years of exploitation is a great tribute to the versatility of the azo chromophore.

Perhaps it is to the intermediates field that we should look in the hopes of a completely novel break, something like the $\beta$-hydroxynaphthoic arylides for example, but in such speculations it is always well to remember that there may be in the dyeing of the common fibres certain governing

limitations, well known empirically, but imperfectly understood as yet. In the case of dyes well suited to wool, development dragged slowly in the early days of the synthetic dye industry, and the position of the natural dyes in regard to this fibre was little affected right up to the commercial synthesis of indigo. It looked as though the wool dyer was waiting for the discovery of a new technique of application. The sulpho group proved to be the key, which not only conferred solubility and substantivity on dyes, but unlocked the immense potentiality of benzene and naphthalene chemistry for providing intermediates for azo dyes. Only a fraction of this potentiality has been used as yet, which is fortunate if there is anything in the speculation that the dye technologist is somehow or other bound to the sulphonic acid group. It may or may not be significant that, even with the only great dye class which is applied otherwise than as the anion—

$$\text{Chromophore–}SO_3^-$$

namely the vat dyes, application difficulties drove the dye chemist to the introduction of the $-SO_3H$ group as in the Indigosols and Soledons.

All of which forces one to expect nothing spectacular in the future of the wool dyes. On the other hand, there is plenty of material on which to base the intensive development of current trends and lines of research.

What the industry needs for its future development is a supply of young men capable of keeping one eye on the ever-widening arch of our knowledge of organic chemistry, with its rich fund of ideas and synthetic methods, and the other on the technology of dye application in order that they may grasp the problems of the user and diagnose them properly. They will find that there is no lack of research targets.

## Concluding Remarks

I hope I have not bored you by my excursion into the history of the wool dyes. I found it a fascinating task myself when I began to sort out the threads, though what I discovered must, I expect, be quite familiar to a number of people who have the historical instinct and can remember dates. I never could do that, and, besides, contemporary events have, during my active life in the industry, absorbed all my attention, what with two world wars and the entire economic reorientation of dye production. Now that these turbulent years are receding, I have found the history of the industry a fascinating study, though what I have been able to offer to you may appear rather elementary. This was brought home to me when, hunting through some old papers the other day, I came upon an essay which I submitted for a college prize in my student days forty-five years ago. It was entitled "The History of the Coal Tar Dyes". I hope I am not guilty of repeating my own juvenalia!

To be quite frank, I was a bit nonplussed when I came to review dye history from the point of view of the dyeing of one particular fibre. Though a Yorkshireman, having the highest respect for wool and its ways, I found it disconcerting to discover, when splitting up my subject into suitable periods or epochs, that each was dominated by a discovery which was primarily of interest in connection with some other fibre, cotton, of course, stealing most of the thunder. By comparison with the great discoveries which have from time to time had a revolutionary effect on cotton dyeing, the wool dyers present a picture of slow, steady progress, fighting a dogged battle against the natural colouring matters. But I never found the subject dull and I am glad if it has been of some interest to you.

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[3] Kruyt, H. R., *Chem. and Ind.*, 260 (7th April 1951).
[4] Knight, A. H., J.S.D.C., **66**, 34 (Jan. 1950).
[5] "Report of the Committee on the Dyeing Properties of Wool Dyes", reprinted from J.S.D.C., **66**, 213–221, 327, 376 (1950).
[6] "First and Second Reports of the Committee on the Dyeing Properties of Direct Cotton Dyes", reprinted from J.S.D.C., **62**, 280–285 (1946), and **64**, 145–146 (1948).
[7] Ris, H., Stocker, W., and Thommen, E. W., J.S.D.C., **64**, 297 (1948).


## Discussion

Mr. C. O. Clark: From Mr. Baddiley's introduction to this paper we rather gather that wool lagged behind cotton in the use of synthetic dyes. Yet two dyes which dye wool from an acid bath, picric acid (*C.I.* 7) and Pittacal (*C.I.* 725), were both known and used before Perkin discovered Mauve. The trouble is that the term "first synthetic dye" is now being used when what is really meant is "the first dye derived from coal tar". We must keep a careful watch on our terminology. Pittacal was derived from beech-wood tar in 1834, twenty-two years before Perkin derived Mauve from coal tar. To recognise that there were synthetic dyes before Perkin's time does not detract from the honour due to him as the first man to derive a colouring matter from coal tar and as the founder of the modern dye industry. We must remember, too, that the word "synthetic" is not exclusive to organic compounds: many inorganic dyes and pigments are truly synthetic, including some that were in use before any synthetic organic dye.

Dr. E. R. Trotman: The direct dyes have been studied and classified very satisfactorily from the point of view of the user, but there does not appear to be such detailed knowledge available about the wool dyes. This appears to be a field of research which requires attention and which would help the practical dyer and should also assist the dye chemist.

Mr. A. H. Knight and Mr. G. S. J. White*: Whilst it is probably true to say that there is less published work in scientific journals on the dyeing behaviour of specific wool dyes than is the case with specific direct cotton dyes such as Benzopurpurin 4B and Chlorazol Sky Blue FF, a great deal

* Communicated

of published information on the different classes of wool dyes and their dyeing properties is available, both in the scientific literature, as exemplified by numerous papers in the Society's *Journal*, and in the pattern books and circulars issued by dye manufacturers. The classification of wool dyes into the levelling (e.g. Lissamine and Naphthalene), milling (e.g. Coomassie and Carbolan), and mordant (e.g. Solochrome, Solochromate, and Neolan) classes has involved the same kind of experimental approach in the way of investigation of dyeing behaviour and affinity as has been employed with the direct dyes. Illustrations of the ways in which chemical constitution can affect the dyeing and fastness properties of wool dyes have been given by A. H. Knight[4].

The problems involved with wool and its dyes are probably more complex than with cotton and the direct dyes, as wool is a much more complex fibre than cellulose. Nevertheless, this has not precluded even a thermodynamical approach to wool dyeing as instanced by the work of Gilbert and Rideal. Workers, past and present, in the various departments of Leeds University which have been associated with work on fibres and their coloration have made major contributions to the phenomena underlying the dyeing of wool. The names of Rowe, Speakman, and Astbury and their co-workers are very prominent in this connection. A perusal of Dr. Vickerstaff's recent book[2] will show how extensive is the literature on the dyeing of wool with both the straight acid dyes and the metallisable or metallised classes.

Finally, the Wool Dyes Report[5] makes recommendations on the testing of acid wool dyes with a view to determining their dyeing and migration properties. The investigations leading to these recommendations were carried out as a direct follow-up of the publication of the Direct Cotton Dyes Report[6].

Mr. J. Holt: The classification of wool dyes according to dyeing properties was dealt with in a lecture by Dr. Ris[7].

Dr. R. L. Elliott: Concerning new chromophores, such as that typified by the phthalocyanines, is it possible that the new work on synthetic tropolones may give a great impetus in the azo dye field?

Mr. Knight: Whilst feverish activity is taking place all over the world on the subject of the chemistry of the tropolones, there is little evidence at present that it is leading to any startling innovations in azo dye technology. Unless the seven-membered ring system on which the tropolones are based furnishes dyes having some novel and technically worthwhile properties in comparison with available products built up from benzene or fused six-membered rings, it is unlikely that it will be commercially exploited in the field of dyes in view of the difficulties attendant upon the preparation of tropolones.

Mr. H. A. Turner: I should like this Conference to know how much I, personally, have appreciated the remarks made by Mr. Baddiley on the subject of training men for the industry in the early part of the speech which has been read to us this morning.

Coming from one who for so many years showed a peculiar genius in selecting, organising, and inspiring scientific and technical workers of many kinds and degrees, I take this as powerful and much-needed support for those principles to which many of us engaged in the training of young men for our industry have tried to adhere, and for those convictions which have developed in us from the experience we have gained during the prosecution of our professional duties. The statement of his own beliefs, so gracefully and so cogently expressed by Mr. Baddiley, will sustain us in our efforts for the future.

As I see it, there is no essential conflict between the methods we favour and either what I may call the purely academic or the purely empirical methods of preliminary training, but, with the author, I feel that the *via media* represented by organised technical education takes greatest account of the present needs and conditions of the industry.

Mr. J. Boulton: The references made in Mr. Baddiley's introduction to technological education are most timely. To-day's issue of the *Times* announces that the Government has accepted the report of its Advisory Committee which recommends the setting up of a Royal College of Technology.

In the introduction to my own paper I pointed to the essential identity of the scientist and the technologist in our industry. In telling us that the technologist must be equipped to keep one eye on the fundamentals of his processes and the other on the application of his products, Mr. Baddiley has given support to that identity, which must find its first expression in the training of our industrial scientists, i.e. in the teaching of technology alongside fundamentals.

Reference has been made at this Conference to many famous research schools, and there is no doubt that British Universities have an unexampled record in the training of young men in the pursuit of knowledge for its own sake, an essential pursuit in any civilised community. But the problems of industry cannot be solved until they have been *posed*, and the young industrial scientist, to be effective, should be able to ask the right questions and be capable of breaking down a technological problem to discoverable fundamentals. To satisfy these requirements he must have the essential mental equipment. The teaching of technology aims at ensuring that he acquires that equipment and does so as part of his education proper. The pure scientist coming into industry must somehow acquire an insight into technology before he can be effective. For example, no young graduate is of much help in a dyehouse for his first five years. As far as research is concerned, an innate ability to pursue ideas is the first essential, and education is secondary. But we must at all times fertilise our laboratories, as well as our

works, with young men to whom the technology of their chosen industry does not provide a mental barrier to be surmounted the hard way.

Mr. J. HOLT: Under present economic conditions, with the necessity of developing continuous and quicker methods of dyeing, has any attempt been made to attack this problem from the dye-making side by producing ranges of dyes which will give quick dyeing times? On cellulose, of course, this problem has been approached from a completely different angle, the Standfast process being ideal as regards speed of production, but it will be interesting to learn if there is any possibility of the problem of quick dyeing on wool being approached from the dye constitution angle.

Mr. KNIGHT: As far as I know, there is no chemical basis on which the problem could be solved.

# The Evolution and Development of Dyeing within the Carpet Industry

G. Robinson and D. Jagger

The dyeing processes of antiquity employed in the Oriental rug-weaving centres are described, and developments in this country of dyeing methods and equipment reviewed. The significance of the various operations employed in the production of hank-dyed and predyed carpet-pile yarns is discussed. Mention is made of several factors peculiar to the carpet industry.

The development of carpet weaving, which is believed to have originated in Southern Persia about 5000 B.C., presents a fascinating study. The shepherds there probably spun coarse yarns with the aid of distaff and spindle and later dyed the coarse yarns into a few simple shades using the juices of plants. The dyed yarns were subsequently woven on a frame into rugs required for protection against the weather, for sitting and sleeping purposes, and as coverings for door and window openings.

At the time of the first written records concerning carpets (A.D. 651), considerable progress had been made in colour, design, and texture. In the East at this period carpets were used as wall hangings for decorative purposes, and in the form of prayer mats for devotional kneeling. The secrets of the craft had been carried across Southern Asia to China and Turkey by nomadic tribes, wandering over the vast areas of upland country which provided grazing for herds of sheep, goats, and camels.

Knowledge of the methods employed by the early Oriental dyers is very limited, because recipes and tricks of the trade were handed down from generation to generation by word of mouth. In some parts of Asia wife worked for husband in carrying out the weaving. The husband assisted with the handling of the wool and in spinning, and he was also responsible for the dyeing of the wool and the provision of the various colouring matters required. On land nearby he had a vineyard, and grew wheat, vegetables, and plants to provide him with colouring matters. Further afield he collected berries and flowers, vallonias and gall nuts, etc., later to be used in the preparation of various decoctions for dyeing.

In this manner, through the centuries, the Oriental dyer acquired a traditional knowledge of natural dyestuffs, their methods of application, and how they stood up to sun and rain. He made use of many mordants and assistants, e.g. pomegranate rind, sumac, bark of many trees, alum, argol, iron salts, etc., and his methods of building up to shade were closely guarded secrets.

The colourings and designs of sixteenth century Persian carpets, of which many examples may be seen in museums and collections, have not been surpassed and provide visible evidence of the skill of the Oriental dyer. At this time there were several important carpet-weaving centres in the East, each famous for the distinctive features of design and construction of the carpets produced there. In these large rug-weaving centres dyeing was carried out independently of weaving, and a number of dyehouses, managed by master dyers each having his own specialities, catered for the various weaving establishments. A dyer of reds was master of his craft, closely followed by a dyer of blues, and the dyer of blacks came last.

The dyehouses were ranged upon the banks of a stream, or else, when suitable water was not at hand, systems of earthen pipes brought water from a stream in the hills into a large basin in the middle of a square, around which were the dyehouses. Copper kettles were used for heating purposes, and dyeing was carried out in numerous earthern jars. The dyeing process consisted of a gradual build-up of shade by a succession of dips in different decoctions. The skeins were allowed to drain between dips, and finally hung out over the flat roof to dry in the sun.

Reds were obtained with madder, alum, and grape juice. Kermes produced a rich carmine, and later was largely replaced by Cochineal, which gave brighter shades. Indigo has been used from an early date for blues dyed from a fermentation vat, and forms the basis of numerous shades including greens. Yellows were dyed with Persian berries, Turmeric, Saffron, and Sumac. Browns were obtained in various ways, e.g. light browns with Madder and a yellow topped with indigo, and darker shades were obtained on an indigo bottom. Gall nuts and Catechu were also used. Blacks were dyed with iron, vinegar, and pomegranate rind. For many drabs, greys, and creams, naturally coloured wools or hairs were employed as far as possible.

Mumford [1] gives the following vivid portrayal of an Oriental dyer of the period immediately before the introduction of coal-tar dyes into the East—

> Traversing a village street in the East you are aware of the dyer from afar off. Red or green or purple from head to heels he challenges sight when he is yet half-a-mile distant. There is the pride of a sultan in his carriage, and in his soul, it is plain, a chromatic joy which religion cannot give. He is a fine bit of colour against the tame background of the town. In baggy knee nethers and white camisole, his head all swaddled in a mighty turban and his fat leathern pouch for pipe, tobacco, knife, money and trinkets, belted about his middle, he is a type. But add to this his dye, which in many values of the same colour illumines him, from the crown of his turbaned head to the tips of his bare toes, and he is a radiant being such as Occidental civilisation has not known, save upon circus days.
>
> In his own view, he is the uplifter of an otherwise slavish and mechanical craft. Through him weaving becomes an art, and all the processes, from first to last, are merely incidental to the main affair— his colouring of the yarns. So he dips and struts his complacent life away, and to be an "al boyaji"— a dyer of reds— is to be one beloved of the Prophet.

The fame of Oriental carpets spread to Europe in the early centuries of the Christian era, and the Saracens invading Spain from North Africa introduced the craft of carpet weaving into Western Europe. The returning Crusaders brought more

knowledge from the East, but Eleanor of Castile on her marriage to Edward I in 1254 is believed to have brought the first carpet into this country. Carpet weaving began in England in the sixteenth century as a result of knowledge gained from the Orient by our adventurous seamen. Carpets were made under the patronage of royal princes and barons, and the few examples remaining are heraldic in design[2].

Carpet weaving in France, along with other industries, suffered a decline in the seventeenth century, and Louis XIV ordered Colbert to remedy this state of affairs. The standard of workmanship of the dyers had fallen, and Colbert after a thorough investigation specified reliable procedures which were to be followed, and the State guaranteed the quality of the dyed goods. The use of some Indigo was permitted, which hitherto had been forbidden in order to safeguard the woad industry; Madder, Kermes, Cochineal, and Weld were among the dyes approved. Colbert is credited with having uplifted the industry, but it is of interest to note that in course of time his regulations retarded development.

After the revocation of the Edict of Nantes in 1685 many Huguenot dyers and weavers sought refuge in this country and settled in London, Wilton, and Salisbury, where they were responsible for a rapid development of carpet weaving. In 1699 the carpet weavers of Wilton received a charter.

At this time dyeing, like hand loom weaving, was a cottage industry, and dyeing was usually done in an outbuilding. The dye vessels consisted of wooden tubs, which were often partly sunk into the ground. These vessels had no means of heating, and hot water was provided from a built-in copper or "set-pan" heated over an open grate.

The period 1750–1850 was one of great industrial development in England, during which there was a remarkable increase in population, from 6¾ millions in 1760 to nearly 18 millions in 1851, compared with an increase of 1¼ millions in the previous 70 years; the population of England in 1688 was 5½ millions. The spinning inventions of Hargreaves, Arkwright, and Crompton, coupled with Watt's invention of the steam engine, soon led to much greater productivity. In 1785 Watt and Boulton used a steam engine to drive a cotton mill in Popplewick, Notts. These mechanical developments caused much heavier demand to be made of the dyer, and the efforts made to meet this demand brought dyehouses into existence.

In 1791 Berthollet[3] made reference to the development of dyehouses, but he omitted to describe them in detail. Some of his observations read as follows—

> We ought to encourage extensive works in dyeing: and those who direct them ought to lay down a plan of operations which might connect the whole, and prevent all loss of ingredients, of time, of fuel, and of work.
>
> It would be necessary to enter into a very minute detail if I undertook to describe everything necessary in the construction of a dyehouse. More accurate ideas may be at once gained by inspection, than the most laboured description could convey. But it is to be wished, both for the progress of the art and even of the science, that a little place should be reserved for keeping an apparatus for the common experiments of chemistry as well as for particular experiments relative to dyeing.

Berthollet mentions cauldrons for dyeing, built from copper or brass except for scarlet, where tin is preferred. He suggests that a succession of cauldrons which require different temperatures be heated by a fire at one end, and the flame and heated air be carried through a horizontal flue to the chimney. The heat communicated to the chimney should be employed by locating the stoves

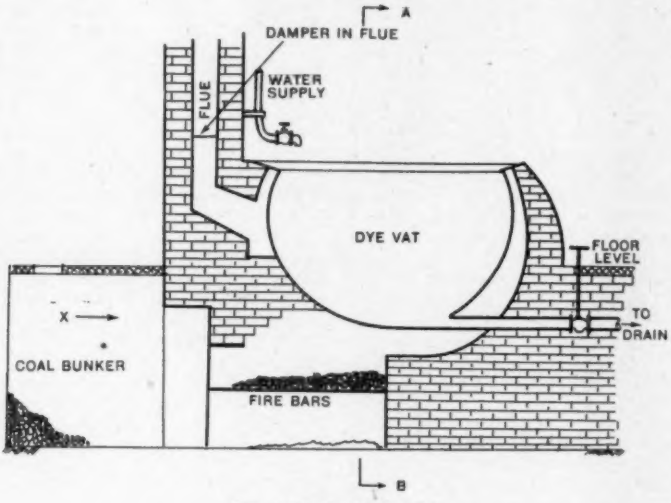


FIG. 1— Fire-heated Dye Vat

and dyeing rooms about the chimney. Wood appears to have been the fuel commonly employed at this period, and pit coal was just coming into use. Berthollet states—

> It is probable that the price of wood will continue to increase and on the contrary that the price of coal will diminish.

Dyehouses for carpet yarns in this country apparently developed on similar lines; old drawings at a Kidderminster works illustrate "furnaces", as they were then termed, heated by a fire and having a flue passing beneath, dividing at the back to return along either side, and finally joining a common flue leading to a chimney stack. The use of fire-heated vats declined only gradually; fifty years ago many remained in use, and even to-day there are a few isolated cases of their use.

An old dyehouse containing four fire-heated cauldrons is still in existence at the Henry Fawcett, Leeds, branch of the Yorkshire Indigo, Scarlet & Colour Dyers Ltd. Fig. 1 and 2 show diagrammatically the general arrangement of one of them

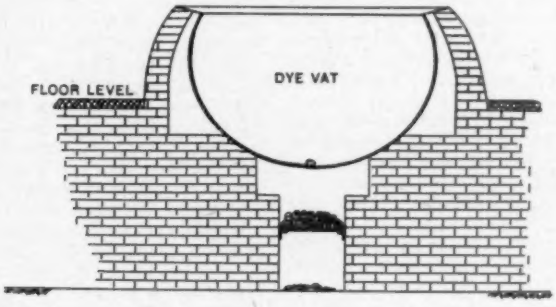


FIG. 2—Section on *AB* viewed from *X* (Fig. 1)

which was in use as recently as 1945. The cauldrons, which are made of copper, and are 10 ft. in diameter at the top and about 6 ft. deep, dyed a load of 200–250 lb. of loose wool. The liquors required about 1½ hr. to come to the boil, and unfortunately no data of fuel consumption are available. When boiling, owing to the curved shape of the cauldrons, the surface of the liquor assumed a conical shape, about 2 ft. in height at the apex, and by boiling vigorously it was possible to form a cone 6 ft. in height without any liquor splashing over the rim of the cauldron. The vigorous circulation of the liquor enabled hand poling to be practically dispensed with, and the dyed stock was lofty and well penetrated. Apparently the stoker was very adept in regulating the degree of boiling according to summary instructions "from above", and in quickly drawing his fire immediately a lot came on shade.

In 1803 Benjamin Gott[4] of Leeds heated the vessels in his dyehouse with steam, generated in one or more boilers on a plan suggested by James Watt, and thereby reduced the number of dyehouse chimneys from forty-two to one. The reference suggests that Mr. Gott had a number of fairly large vessels, which previously had been each independently heated by an open fire. The use of steam as a source of heat or power does not appear to have spread rapidly, and it is a little over a hundred years ago since steam power was applied to carpet manufacture. No record has been found of the initial use of steam in a carpet yarn dyehouse, but steam-heated vats were in use about 1865.

In 1882 steam had come into more general use, and in that year the following reference[5] appears—

> Dyeing vats or coppers are heated directly by a furnace or by means of steam conducted in a pipe from a boiler at a distance from the vat. In the first case the vessels are almost always made of copper, only in special cases, for the scarlet and some delicate silk dyes, of tin, in the second case they are of copper, iron or wood. Madder and Indigo vats when heated by steam have it either admitted directly into the liquor, or made to circulate by pipes plunged into it or placed between the copper and an exterior iron or wood case.

In England during the eighteenth century, Indigo gradually displaced woad. Madder, Kermes, and Cochineal (the latter now dyed on materials mordanted with tartar and scarlet spirits) were widely used. Several American dyewoods, e.g. Logwood and Fustic, became available; later these were offered in a convenient form rasped or chipped, and finally as liquors or extracts.

A dye recipe book, dated 1849, of Moses Whittall, carpet manufacturer of Kidderminster[6], contains samples of woollen yarns, of which examples are dyed according to the following recipes—

| 60 lb. FAWN | 120 lb. GOLD | 60 lb. RED |
|---|---|---|
| 10 lb. Madder | 6 lb. Tartar | 7 lb. Argol |
| 4 oz. Copperas | 3 lb. Fustic | 12 lb. Lac |
| 4 oz. Logwood | 2 lb. Alum | 3 quarts Lac spirit |
| 2 lb. Fustic | ¼ lb. Grain | |
| ¼ lb. Cudbear | 6 quarts spirit | |

The discovery of chromium salts and the realisation of their effectiveness as mordants had far reaching effects. The introduction of the use of sulphuric acid early in the nineteenth century

had similar results, although its use developed only gradually, and an early use was in the manufacture of indigo extract.

A dyers' handbook[7] published in 1875 contains many examples of shades dyed on 3% chrome-mordanted wool, e.g.—

FRENCH BROWN (50 lb. wool)

| | | |
|---|---|---|
| Preparation— | 1½ | lb. Chrome |
| Dyeing— | 6½ | lb. Fustic |
| | 1 | lb. Madder |
| | ½ | lb. Cudbear |
| | 1 | lb. Tartar |

The long and tedious methods of application of natural dyestuffs, which had persisted since ancient days, gradually fell into disuse after Perkin's discovery of Mauveine in 1856, but it was not until towards the end of the nineteenth century that coal-tar dyes became widely used in England for carpet yarns, owing to the fugitive nature of the early members.

Very few of the recipes in the handbook[7] employ coal-tar dyes, such as Safranine, Aniline Orange, and Aniline Green. Fields or Blackley Orange (Aniline Orange) is stated to give good results on wool, used sparingly and at good heat with a small addition of acetic acid. During the following ten years Acid Magenta, Roccelline, Naphthol Yellow, Acid Oranges, and the earlier Acid Scarlets were used.

It is of interest to record that the introduction of coal-tar dyes into Persia, although simplifying the dyeing procedure and making brighter shades possible, led to serious deterioration in fastness of the shades dyed, to light and water. In the year 1900 the Shah of Persia issued an edict[8] forbidding the importation or use of coal-tar dyes under the threat of severe penalties and confiscation of goods, but the edict was of short effective duration.

The carpet industry in this country continued to use natural dyestuffs well into the present century, but from the beginning many level-dyeing acid dyes were in general use, e.g.—

Naphthol Blue Black
Patent Blues
Acid Oranges
Acid Greens
Fast Green Bluish
Wool Green S
Azo Fuchsine
Fast Reds
Carmoisine
Acid Scarlets
Acid Violets
Tartrazine types

During the next few years Amido Naphthol Red G and Xylene Light Yellow 2G were introduced; both were very level dyeing, the former being faster to alkalis than earlier acid reds, and the yellow giving good fastness to light. For many years these two dyes together with Patent Blue, Fast Green Bluish, or Wool Green S provided a three-colour combination for the carpet yarn dyer. Alizarine Sapphirol B only came into general use following the first world war, when manufacture began in this country.

During recent years an increased fastness to light has been obtained by the use of Acetyl Fast Red BG or Lissamine Fast Red BS types along with Kiton Fast Yellow 2G and Alizarine Brilliant Blue BS. Solway Blue PFN finds increasing use in order to give greater fastness to urine or salt spattering.

For dark browns Tartrazine N or S is used to some extent as the yellow component, and Orange G appears to find a limited use for shading purposes or as a basis of dark browns. Kiton Red 6B, Carmoisine W, and Fast Acid Scarlets are in general use, and blacks (often supplied as mixtures) are based upon Naphthalene Blue Black along with Orange II and an acid red.

Bright greens present a problem, and a greater or smaller proportion of Erio Green B is used according to requirements.

In special cases, e.g. yarns required for carpets of ships, restaurants, railway carriages, etc., where a high standard of fastness to wet influences is required, Neolan or Ultralan dyes are used, but the range of shades possible with the use of these dyes is inadequate, particularly in brightness. The metallised dyes are suitable also for yarns used in carpets which are to be given a hypochlorite after-treatment to produce an enhanced lustre or antique effect in imitation of an old Persian rug.

The reasons for the choice of level dyeing or equalising acid dyes are apparent after a consideration of the practical requirements. Most firms have their own dyehouses, and several carpet manufacturers carry out the entire processing from raw wool to finished carpet. The large number of shades and the large weights involved make this course desirable. The larger dye loads are usually intended for use in plain carpets and the ground shades of patterned goods, where levelness and thorough penetration are essential. Developments in yarn-dyeing equipment will therefore be briefly discussed.

During the latter half of the nineteenth century, following the introduction of steam for heating purposes, carpet yarns continued to be dyed by hand in open vats, constructed of pitch pine or Columbian pine. Hanks were suspended on dye rods 2 in. square, each holding six dolls, two ½-lb. hanks slightly twisted together forming a doll.

Vats of 120 lb. and 60 lb. were in common use together with smaller units. The hanks were turned by two workmen, one standing at either side of the vat, who gave five or six turns whilst heating to the boil, and three or four turns at the boil. The men became very skilful, and not only transferred the end sticks to an inner position, but also slipped the outer dolls to the middle of the sticks. Later, vats of up to 400 lb. capacity were in use, and required four men for turning. Towards the end of the century machines were introduced which gave a mechanical movement of the yarn during the dyeing. One type of machine, fitted with lifting gear and clamps over the stick ends, periodically raised and lowered the sticks several inches. The Partridge machine gave forward and backward motion to the yarn, and later machines had arrangements for rotating the sticks.

The Klauder-Weldon machine, which followed, consists of a vat carrying two parallel vertical wheels between which rows of hanks are carried on two sticks clamped horizontally, one close to the axle and the other close to the periphery of the wheel. During dyeing, the wheel slowly revolves, and at each revolution a mechanical arrangement causes the sticks to be given a quarter turn. Slightly more than half the wheel load is above the liquor, and therefore the machines are enclosed to reduce the cooling of the yarn, etc. The Klauder-Weldon gave very good results from the points of view of both levelness and the condition of the yarn after dyeing.

The Hussong machine came into use about 1908 and employed a different principle, namely that of circulating the dye liquor instead of moving the yarn. The use of this machine soon spread throughout the carpet trade, and machines of this type of capacity up to 1 ton are now in regular use. In some cases by the use of "linked" machines higher capacities are obtained. The dyes employed must have good level dyeing and penetrating properties and be free from insoluble matter, which could be filtered out by the yarn during the circulation of the liquor. The Hussong machine consists of a rectangular vat having a baffle plate or partition towards one end, forming a compartment in which a propeller is fixed. The main compartment is fitted with a false bottom, containing spacings in the case of wood, or perforations in metal, which increase in effective area with distance from the propeller end of the machine. The hanks of yarn are suspended on rods fitted into a frame beneath a false top, with a lid above. When the frame carrying the yarn is lowered into position, the baffle plate extends between the false top and false bottom, i.e. it does not reach to the top or bottom of the machine. During operation the propeller forces the liquor to circulate under the baffle plate, upwards through the yarn, and back to the propeller box, or the direction of flow may be reversed. The machine is so designed that a uniform circulation takes place throughout the yarn.

Hussong machines were originally made of pitch or Columbian pine, or cypress, the last mentioned having the longest life. Some machines carried a double frame of yarn and two propellers, while others had a propeller at each end. Light shades could not be dyed after dark ones owing to the marking off of dye retained by the wood. Since 1930 there has been a gradual changeover to the use of machines constructed of stainless steel. Early types of stainless steel vats were unsatisfactory because they were subject to weld decay and the metal used was too thin in gauge. Trouble was also experienced owing to the acid liquor getting behind the timbers of the supports and causing corrosion to take place from the outside of the tank. Modern machines in thicker gauge stainless steel or similar metal fulfil the requirements of carpet yarn dyeing, and wooden machines are rapidly diminishing in number.

Several modifications in the design of Hussong machines have been made during recent years. In one machine the hank-supporting frame is fitted with vertical side plates which permit a heavier loading; the false bottom is dispensed with, and a stronger circulation of liquor is given. Specially shaped dye sticks are used which offer a minimum area of surface contact with the yarn as a safeguard against stick marking.

Many modern machines are now fitted with time-temperature controllers (Fig. 3), whereby every dyeing may be begun at a specified temperature and the liquor brought at a uniform rate to 210°F. and maintained at this temperature. In this way too rapid heating and the danger of boiling over are avoided. It is usual to maintain the liquor at 210°F. in view of day-to-day variations of barometric pressure, but if desired a delicate upper-limit control may be set to give the degree of turbulence required.

At the commencement of dyeing the machine is prepared by dissolving the dye by "boiling up" in the machine about a quarter filled with water. This method of dissolving is necessary owing to the large weight of dye often required, which makes it impracticable to dissolve it in a separate receptacle. The machine is then filled to the correct level with water, and 10–15% Glauber's salt and 3–4% sulphuric acid are added. Steam is turned on and the propeller set in motion; when the specified commencing temperature (usually 110°–120°F.) is reached, the previously wetted-out and "sticked-up" yarn is lowered into the machine. The liquor is brought to the boil in 45–60 min., and maintained thereat for 60–90 min. The steam is then shut off and the circulation stopped; then the yarn is lifted clear of the liquor, and a sample taken for matching purposes. After the addition of any further small amounts of dyes required, the yarn is lowered, and dyeing continued for a further 20–30 min.

Formic and acetic acids are used to a limited extent for the less level acid dyes, and phosphoric acid has also proved to be useful, particularly in cases where iron is present in the water supply. After the completion of dyeing the yarn is usually removed from the machine and hydroextracted and dried without rinsing, but in some cases the dyed yarn is either washed off in the machine or hosed during hydroextraction. Drying without rinsing is considered to give a slightly harsher yarn which produces a firmer carpet pile, and the dyeings are a little faster to water. No doubt the nature of the water supply available has some bearing on the procedure adopted, since slightly alkaline waters are apt to cause a slight bleeding of some heavy dyeings.

As previously indicated, only fast, level-dyeing acid dyes appear to be in general use both here and in other countries, and so far as we are aware no firm has found it practicable to employ acid milling dyes owing to the high standard of levelness and penetration required. Occasionally acid milling dyes are used for "top colours" in cases where a high degree of wet fastness is of greater importance than absolute levelness, e.g. the dyeing of bright shades which are unobtainable with metallised dyes. Similarly a full shade, intended to form

a small portion of a design but working against a delicate ground shade, may be attempted.

The standard of light fastness obtained appears to meet requirements, since very few complaints of fading arise; furthermore, day-to-day observations of the colourings of the carpets in household or hotel use seldom show any noticeable fading. It should be appreciated that the delicate fawns and creams when dyed upon a slightly yellow ground have a tendency to lose yellow on exposure to light, owing to the fugitive nature of the natural pigment of the wool. In these circumstances a more balanced fade is obtained by the use of a very fast-to-light yellow, fortunately available in the form of Xylene Light Yellow 2G, along with red and blue of lower fastness. This is the opposite of what is done in the worsted industry, where a very near white ground is used which tends to yellow slightly with exposure.

Carpets differ from most other textiles in that immediately they are put into use they are exposed to continual deposition of dust and to being trampled underfoot; consequently, a varying degree of soiling takes place according to the conditions of wear. These conditions result in an apparent loss of depth of shade, owing to the pressure marks termed "shading".

When a new carpet is laid the tufts are almost vertical; they lean very slightly, but all slant in the same direction, and therefore only the cut ends of the tufts are visible at the surface. After some wear the tufts gradually assume a greater slant, thus exposing the sides of the yarn to view. These reflect light to a much greater extent than the "cut ends", and consequently the carpet appears lighter, particularly when viewed in the direction of the lie of the pile.

In general, carpets containing worsted yarns are more liable to "shading" than those containing woollen yarns. It is, of course, more noticeable in plain carpets than figured goods, because in the latter the design distracts attention from the shading.

The presence of dust on heavy shades, e.g. dark blue and black, has a slight greying action.

With regard to fastness to wet treatment, it is seldom that bleeding of dye occurs, and in such cases the matting and distortion of the pile, due to the saturation and cleaning, cause greater unsightliness. There is a need for a blue dye comparable with Solway Blue B or PFN but having an excellent fastness to saline influences, which would obviate the formation of discolorations arising from urine, etc.

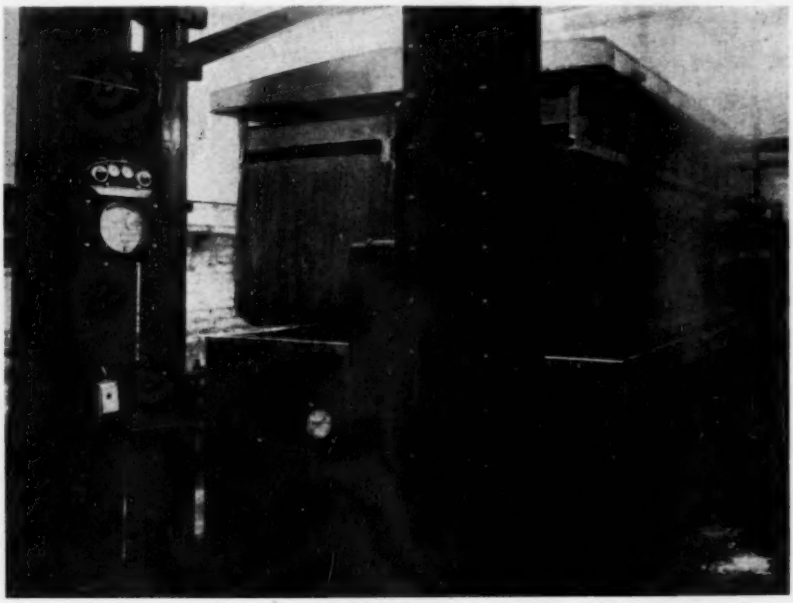

FIG. 3

The standard of matching is very high, owing to the carpet designs containing sets or groups of shades differing in steps of hue or depth. Very little latitude is permissible in ground shades, otherwise the balance of the colouring of the design is disturbed. In large establishments 2000 or more shades may be in current use, which include delicate tints and heavy rich shades which reach the limit of the affinity of the yarn for dyes. Matching is usually carried out by comparing a "cut tuft" of the dyeing against a standard, except

where the yarn under consideration is required for Brussels, i.e. uncut or "loop-pile" carpets.

The popularity of plain carpets, particularly in dollar-earning markets, culminating in a call for seamless or broadloom carpets to cover entire floors, and embracing sculptured or carved styles and other novel weaving effects obtainable by the use of high and low wires, cut and uncut, presented many dyeing problems. The demand for many difficult shades, e.g. silver grey and a very deep wine, necessitated careful control of processing methods.

Hank dyeing of large weights of yarn required for the production of plain goods, particularly in broadloom, is not entirely satisfactory for several reasons. A consistently high standard of levelness and matching must be maintained in order to produce a high-grade carpet fit for export. It is virtually impossible, and certainly not practicable commercially, to dye successive lots of yarn to match one another exactly, and thus enable them to be used indiscriminately in the same weaving, or if used separately for the carpets so produced to match when laid side by side. For these reasons during the last quarter of a century the use of loose-wool dyed stock, blended before spinning, has steadily increased.

This procedure consists in dyeing blends of 5,000–50,000 lb. weight. The blend is finally adjusted to shade on the colour-matching principle as used in the worsted trade. Before giving further details of the dyeing procedure, since woollen yarns usually form the pile of plain carpets, some information about the woollen spinning procedure and ancillary operations is required.

Carpet yarn blends are usually a mixture of several wools. In general hill sheep provide the best carpet wool, their fleece being composed of long hairy fibres forming an outer coat and shorter and finer true wool fibres as an undercoat. A small amount of kemp unfortunately is usually present. East India wools are acknowledged to form the best basis of a carpet wool blend, as they confer good resiliency and coverage and wear exceedingly well. The yellow type is considered to produce the firmest carpet pile, but its colour is a disadvantage. British wools, Blackface and similar types, are sturdy and longer in staple, and their inclusion facilitates the spinning of the shorter East India wools. New Zealand wools produce a softer pile and are well suited for closely woven Wilton qualities; owing to their good colour, they provide an excellent basis for the dyeing of pastel shades. Matchings, britch, skin, slipe, etc. wools are useful components, particularly from a cost point of view. Blending is a most important operation and has received much more attention latterly. Bad blending is shown up by the development of streakiness during dyeing, due to differences in affinity, and also by optical effects in the finished carpet brought about by variations in light reflection.

In woollen spinning mills, until the early 1930s it was the practice to process blends in grease with the addition of oleine oil as lubricant. Under these conditions frequent fettling of the carding machines was necessary, and the yarn produced between the extremes of a clean and a dirty card varied accordingly. Towards fettling time an increased amount of solid fatty acids— stearic and palmitic acids— became occluded with earthy matter. The formation of lime soaps, from lime present in the wool, is detrimental because, once formed, they are difficult to remove. These differences have been shown by an examination of the oil extracted from samples taken at the beginning and end of a run, and are demonstrated by a mild scouring treatment, which effectively cleans the first and not the last. These differences were largely overcome by giving a drastic scouring treatment. There appears to be no doubt that many dyeing troubles were due to processing greasy wool, because at the time when a changeover was made to the use of wool washed prior to spinning, this was immediately reflected in a marked improvement in the quality of the dyeing results.

The traditional woollen spinning oil, oleine oil, is generally used, and satisfies spinners' requirements. A good-quality oil of minimum 70% saponifiable matter is usually fed from a thermostatically controlled tank, which overcomes difficulties arising from the settling out of solid fatty acids. Oiling devices are in use to give a more uniform application of oil than hitherto. The fairly strongly alkaline scour required to remove oleine, and the measures necessary to prevent the formation of lime soaps, tend to cause a yellowing of the wool and the risk of residual alkali. For these reasons oleines are now meeting competition from spinning oils having a mineral oil base, which scour out with a mild scouring treatment and do not form insoluble lime compounds. Some types are self-scouring oils, and may be removed by a passage through warm water only. Fire insurance regulations have hampered the development of these products, many of which, at least, present no greater fire risk than oleines, but there are indications that the restrictions concerning their use may be removed.

The scouring of yarns is usually carried out by a passage through a continuous brattice or tape machine. A four-bowl set is common, using two bowls for detergents and two rinsing bowls. Much better control than formerly is now exercised during the operation. Some machines are operated on the counter-current system, with a controlled water supply and continuous feed of detergents, and the liquors are thermostatically controlled. Dolly scouring has a limited use, and two or three machines are used in parallel for scouring and rinsing. The use of the same liquor "topped up" for successive batches may lead to dyeing troubles, owing to an increase in soap and alkali residues.

Returning to the preliminary remarks on loose wool dyeing, the changes in procedure necessary as compared with dyeing in yarn form may now be considered. Before loose wool is dyed, it must, of course, be well washed. This is accomplished in the usual types of wool-washing machines. The synthetic types of detergents have to some extent replaced soap, and give very satisfactory results,

besides being more economical, especially when washing limey wools or using a hard water supply. The wool is well shaken to remove as much earthy matter as possible and to provide a more open wool to be washed. After washing, the wool is dyed in loose stock machines of 400–600 lb. capacity, where the wool remains stationary and the liquor is circulated. In some cases the wool is dried after washing, weighed amounts being taken and rewetted before entry into the dye pans. In other cases the wool is taken direct from the last squeeze of the washing machine.

The choice of dyes is governed to some extent by the subsequent procedure employed. Certain American firms are understood to card and spin the dyed wool with the addition of about 1% spinning oil on the weight of wool, applied in the form of an emulsion, and it is stated that on occasions water only is added. After spinning, the yarn is used for weaving without any further treatment. This procedure has not been adopted here so far as we are aware. The residual oil and grease contents of samples of yarns processed by this method which we have examined are greater than 1%, which may accelerate soiling and result in a carpet surface which is inclined to be "mushy".

In this country the predyed yarns are scoured before weaving in order to leave a satisfactory low grease content, usually about 0·5% residual oil and grease; a fuller yarn is obtained, and any soiling which may have occurred earlier is removed.

Dyeing in the form of loose stock enables faster dyes to be used than in the case of yarn dyeings, indeed the dyes used must be fast enough to withstand the scouring treatment given later. The metachrome, afterchrome, and fast acid milling dyes are used. Apart from the first one or two pan-loads of a new blend, no "salting on" of dyes is given and the dyeings are done to a time schedule until nearing the end of the blend, when final adjustments are made.

At this stage it is of interest to compare the fastness of colours in modern carpets with those of old Oriental carpets, which are sometimes stated to be "as good" as the day they were woven. In the case of the famous Ardebil carpet woven in the sixteenth century (now in the Victoria and Albert Museum, London), this "day" represents 35 years of the life of one Macksoud of Kashan, entrusted with the weaving of this carpet for the mosque of the holy city of Ardebil. Incidentally, this carpet, measuring 32 ft. by 16 ft., contains 380 hand-tied knots per square inch, or a total of over 33 million knots. The colours certainly required to be fast in those days in order to outlive the weaving let alone wearing, nevertheless not all the old vegetable dyes possessed very good light fastness. Shades based on Indigo and Madder have withstood the test of time, but the yellows were undoubtedly fugitive, and only very dull shades obtained by the use of metallic pigments were fast. Consequently in some antique carpets yellows are badly faded and greens have become blues. Many of the darker shades, particularly blacks, have tendered the yarns. The old Persian craftsmen are said to have read patterns blindfold, owing to the changes in handle of yarn caused by the different dyeing procedures.

The dyeing of carpet yarns in package form as far as we are aware is not carried out in this country, although this form of dyeing is being considered. Dyeing on cheese is understood to be in use in the U.S.A., and one firm is stated to use this method for all lots which are too small to be dyed by the stock-dyeing process[9]. It is to be expected that a leaner yarn may be produced by package dyeing, possibly accentuated towards the centre of the package, and this could affect the final "bursting" of the cut pile during the finishing process of the woven carpet. Certain difficulties with regard to scouring on cheese would have to be overcome, and precautions taken during dyeing to exclude the presence of any insoluble matter likely to filter out on to the surface of the cheese.

Development of the dyeing of yarns in package form appears to be bound up with spinning developments leading to an elimination of yarn in hank form; i.e. if, after folding, yarns could be collected on cheese and subsequently scoured, dyed, and dried ready for warping or weaving, this would be of great advantage.

The dyeing of carpet yarns on beam also offers interesting possibilities which have not been lost sight of. Practical trials have given promising results both when dyeing on cheese and on beam. One of the problems associated with this possibility is the drying of the cheeses or beams.

The dyeing of plain carpet can be done satisfactorily in a winch machine, but to the best of our knowledge this is carried out in this country only by firms of dyers and cleaners. One American carpet firm is believed to use this procedure. It is also possible to scour and dye piece goods on beam, and experimental lots have been processed in this way; the backing yarns of pieces suffer a loss in weight and rigidity, and require to be back-sized as a final operation. Continuous dyeing processes offer interesting possibilities, either for the dyeing of pile yarns as a creel-to-beam or beam-to-beam operation, or for the dyeing of woven carpet into plain shades.

Bleaching of carpet yarns is not often found to be necessary, and when required is usually done with hydrogen peroxide. Fluorescent colourless dyes find a limited use in counteracting the natural yellow colour of yarns when dyeing delicate shades, e.g. pale blues, and in such cases a more balanced fade is obtained.

Tapestry carpets, woven with a loop or Brussels pile from printed warp-pile yarns, ranked among the most important carpet qualities until comparatively recently. The printing process consists in wrapping a number of ends of yarn around a printing drum, where they are printed with bands of colour. The operator is enabled to print any colour in proper position upon the yarn as the drum revolves. For each colour printed, a separate colour box is

used, containing a rotating disc, which comes in contact with the yarn during its passage across the drum. After printing, the yarn is loosened and taken off the drum in the form of a large hank, which is next transferred, stretched upon a frame, to a steaming chest. After steaming, rinsing, and drying, the yarn is wound on bobbins, which are all suitably numbered, since each represents the same warp end of pile yarn, subsequently to be mounted in a creel behind a setting frame, as one of a set of bobbins forming the desired pattern.

The printing pastes are prepared from acid dyes with the addition of a thickener and acetic acid. Rice meal (from the rice polishing process) was widely used as a thickener at one time. Other thickeners include gum tragacanth, modified starches, cellulose ethers, sodium alginate, etc.

When weaving tapestry carpets, owing to the tendency of the backing fibres to "grin through", these are usually dyed. The warp backing threads, consisting of chain and stuffer, are coloured by passage through coloured size. The weft yarn is usually dyed on cop and then sized, or dyed and sized in the same operation. Dyeing machines are used where the cops are fitted over perforated spindles, which in turn fit into holes in a large plate or drum. During dyeing, the liquor is forced through the cops by means of a pump circulation. In another type of machine the cops are placed within a pressure container, which is then closed and made airtight. The container is then evacuated, after which the hot dye liquor is entered, and finally dyeing takes place under pressure.

For many years limited quantities of viscose and acetate rayons have been employed as carpet pile yarns. Their use would no doubt have substantially increased during the past twelve months had supplies been freely available. Carpets in patterned goods in both cut and round wire qualities, and also imitation hair cord, have been produced using rayon as pile yarn, but their greater application appears to have been in the form of blends with wool.

The use of blends obviously complicates the dyeing procedure, not only from the points of view of dye selection and method of dyeing employed. Carpet yarn dyehouses were planned for the dyeing of wool with acid dyes, and great care must be exercised in order to avoid contamination of the cellulosic fibres with acid from dyehouse trucks, etc. In some cases the hardness of the water supply available, although not causing undue difficulties when dyeing wool, is unsuitable for the dyeing of cellulosic fibres [10].

Some of the more recently introduced synthetic fibres, e.g. nylon, Terylene, and the various acetylene derivatives, may become regular components of carpet pile yarns. Most of them have great strength and possess hydrophobic properties. These types present dyeing difficulties, and most developments in dyeing technique are based upon a controlled modification of the filament structure by the use of swelling agents to facilitate dyeing. In this respect it should be pointed out that wool is a fibre of only moderate strength, and high-tenacity yarns are not necessary for its replacement in pile yarns; therefore, synthetic types of lower strength but of a more hydrophilic nature appear to be desirable, provided their wet strength is satisfactory.

The regenerated protein fibres, e.g. Ardil and Fibrolane, appear to offer many advantages on account of their wool-dyeing properties, resistance to burning, warm handle, etc., and a considerable use of these fibres is predicted. Both of these fibres are, however, of low wet strength, and on account of this it would not be possible to use them alone. The colour of Ardil, which is expected to improve during the course of the next few months, necessitates a bleaching treatment for the production of delicate shades.

The application of colour-measuring instruments, as in other branches of the dyeing trade, has received much attention, both as an aid during dyeing, and as a means of determining when a match has been obtained within prescribed limits. Their use during dyeing, in order to calculate the additions of dye required to bring to shade, appears to be limited owing to the behaviour of individual dyes during dyeing; e.g. in the usual three-colour combinations the dyes do not exhaust at equal rates, and the red component in particular gradually assumes a slightly bluer tone owing to acid hydrolysis as dyeing proceeds. The tri-chromatic colorimeters have not been found to be sufficiently sensitive to record when a match is obtained, and the visual types are subject to human error. Calculated tristimulus values from the reflectance curves of a spectrophotometer are only useful provided the shades examined appear the same under all conditions of illumination. Therefore this instrument could not assist in extreme cases, e.g. in the match of a green shade produced from a homogeneous green against one from yellow plus blue, or in the case of a grey from blue plus orange against one from violet plus yellow. For these reasons it is concluded that colour-measuring instruments cannot be of material assistance either as an aid to dyeing or for the purpose of defining when a match has been obtained.

* * *

The authors wish to thank Messrs. Carpet Trades Ltd. for permission to publish this paper, and to express their gratitude to Mr. M. V. Campbell and Mr. G. H. Head for helpful discussions.

Carpet Trades Ltd.
Kidderminster

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## Discussion

Mr. A. K. Taylor: With reference to the blending of the man-made fibres with wool for carpet yarns, what is the suitability of Ardil, from the point of view of resilience and durability, compared with the synthetic fibres, nylon and Terylene? One would tend to question adequate resistance to abrasion in the case of Ardil.

Mr. Robinson: Three carpet samples, having all-wool and 75 : 25 and 50 : 50 wool–Ardil mixture woollen-spun pile yarns respectively but identical in other respects, have been subjected to a practical wear test since 1946. In the early stages it was very difficult to differentiate between them by comparing their appearances or by walking over them. Later the surface of the 50 : 50 wool–Ardil carpet became a little more matted than the all-wool sample, but this effect was hardly noticeable on the 75 : 25 wool–Ardil sample.

In another test, carpets having a worsted pile, and employing the same proportions of the components as above, have been laid in a much-used corridor for nine months. The 50 : 50 wool–Ardil appears to be slightly less resilient and less resistant to wear than all-wool, and the 75 : 25 wool–Ardil is only slightly inferior to the latter.

Several types of man-made fibres obtainable in U.S.A. are not available in this country, and others are available only in fine-denier qualities.

The qualities of wool and the filament diameters of the synthetic fibres blended, also the type of yarn produced and the carpet construction employed, influence resiliency and resistance to abrasion. Accelerated abrasion tests provide a useful guide, but they cannot reproduce the effects of variations in humidity and temperature, or the degree of soiling and the cleaning procedure met with during service.

These factors have retarded development in this country, and much work remains to be done before the value of the various synthetic fibres as components of carpet pile yarns can be assessed.

Nylon carpets manufactured in U.S.A. are understood to be resilient and exceedingly resistant to wear. Blends of nylon with wool would be expected to be harder wearing than wool alone, as is found in fabrics or hosiery, and no doubt similar remarks are applicable to Terylene.

Mr. C. O. Clark: If the four cauldrons at Messrs. Henry Fawcett had been fired with gas or oil instead of coal, they would have been remarkably easy to run, but they had gone out of use before such ideas became widespread. The cauldrons went out of use solely because the special bricks used for surrounding them were no longer available, as the only firm making them went out of business. These firebricks— as will be seen from Fig. 1 and 2 they formed part of the flue surrounding each cauldron— were curved and had a tongue at one end and a recess at the other end, so that adjacent bricks in a layer fitted into one another to give a firm structure.

Mr. R. L. Hill: Is there any interest taken in the English carpet industry in the application of screen printing technique for the colouring of plain woven carpeting?

Mr. Robinson: So far as I am aware, it has not been found possible to penetrate to the base of the pile when using screen printing methods; therefore the process appears to be suitable only for carpets having a very low height of pile. A roller-printed carpet has been in production in the U.S.A. for many years. I am not familiar with the details of the procedure used, but the results obtained are quite good, particularly with regard to penetration.

Mr. C. P. Atkinson: Attempts made in 1936–1938 to introduce the use of viscose rayon as a carpet pile were followed up in Kidderminster, while in the North of England and in Scotland the reaction of the trade was only lukewarm.

Mr. F. Illingworth: In the cheese dyeing of carpet yarn is the "burst" affected, and is it a fact that a lean yarn is produced? I have seen cheeses which show no effect of leanness. Experimental work on this point is being done in this country at the present moment.

Mr. Robinson: Cheeses which have been wound too tightly give a leaner yarn, which is most pronounced at the centre of the package, and this results in differences in burst of the pile during finishing. By the use of a correct winding procedure this effect appears to be overcome, and yarns dyed on cheese are used to a limited extent for carpets.

Very careful control will be necessary when dyeing yarns on cheese for plain carpets, otherwise physical differences from any lack of uniformity in winding may result. Similarly, any slight differences in dye absorption between the inside and the outside of the package, or a filtering action on any insoluble matter present, would lead to defective dyeings.

Mr. C. L. Bird: In order to clean a dirty carpet it is necessary to apply some form of wet treatment, e.g. shampooing, but level dyeing acid dyes in high percentages, e.g. as maroons, do not stand up well to such treatments. Does it seem likely to the authors that, in spite of the technical difficulties, carpet yarn dyers will, in the future, be forced to use milling acid and chrome dyes to a considerable extent? Such a state of affairs has been brought about in the hosiery dyeing trade, mainly because of the use of non-felting treatments, which lower the fastness to wet treatments of level dyeing acid dyes on wool. In the carpet trade a similar situation might arise through the use of synthetic protein fibres in admixture with wool.

Mr. Robinson: This question is not entirely unexpected, and the references in the paper give some indication of the attention this matter has received. The importance of levelness of shade cannot be overemphasised, however, particularly in view of the high monetary value of dyeing loads of yarn up to a ton in weight. For this reason I cannot foresee a much greater use of the acid milling dyes, unless the risk of unlevelness is removed by a more reliable method of application, or by the introduction of more easily levelling dyes. The manufacture of metallised dyes of greater brightness would lead to a greater use of this class of dyes.

With regard to the dyeing of mixtures of wool and regenerated protein fibres, e.g. Ardil, the latter is stated to have a large capacity for absorbing acid or alkali. Using dyes possessing a high neutral affinity, if Ardil is dyed in a strongly acid state even from a neutral dyebath, unlevel, badly penetrated results can be expected. On the other hand, if Ardil is alkaline, a poor tinctorial yield is realised from a neutral bath. Therefore the acid milling dyes cannot be expected to be very suitable.

Metallised dyes may be applied by the conventional wool dyeing method and give results of good all-round fastness. Although the wet fastness of level dyeing acid dyes is much lower on Ardil than on wool, this effect is not great when dyeing a wool–Ardil mixture containing not more than 25% Ardil. During the dyeing of Ardil a small amount of formaldehyde is released; therefore certain dyes which are reduced by formaldehyde should be avoided. Carpet yarns are not expected to meet repeated wet treatments like hosiery. In fact, the saturation of an undyed cut pile carpet with warm water alone tends to produce a permanent distortion of the surface. Carpets are usually shampooed using a minimum application of water to prevent this distortion of the pile and to facilitate drying. Many non-alkaline shampoo powders and liquids based on synthetic detergents are available which produce no ill effects.

Bleeding of colours due to accidental spillages is by no means a common occurrence, as is surely borne out by everyday observations of carpets. In most cases spillages leave a stain or discoloration and some distortion of the surface. On several occasions during my experience cases of bleeding, reported to be due to the spilling of water, were confined to a small portion of the wetted area, and found to be due to the presence of coloured substances, e.g. fragments of chalk, lipstick, etc.

Mr. L. J. CLARKE: This point has brought out very clearly a point which has also arisen once or twice before in this Conference, namely the impact of the consumer and designer interests on the technologists and their work. Anyone engaged on the commercial side of the textile industry must acknowledge how frequently difficulties and misunderstandings arise in his attempts to bring about a sympathetic understanding between these two groups, who unfortunately speak different languages.

The scientist hates generalisations, but in aiming at absolute accuracy hedges his statements about with so many qualifications that unfortunately, instead of being credited with the virtue of truthfulness, he is suspected of being shifty and evasive or, as the man in the street puts it, he either cannot or will not give a plain answer to a plain question. The retort that the so-called plain question is, in fact, obscure and muddled does not help to smooth matters. Nor are the Society's publications dealing with colour fastness suited in either form or language for lay consumption, and we must confess that grading fastness by series of numbers which are purely relative, coupled with the inability to state precisely what fastness No. 1 in the series means in terms of usable life, is open to criticism.

It therefore seems to me that the Society, with all the information which it has available from the scientific side, should interest itself in the problem of meeting those more immediately in touch with the consumer world with a view to finding out whether it is possible to devise standards expressed in lay terms which will at the same time avoid ambiguity on the technical side. There are a number of trade organisations in the textile industry which would be only too willing to help in this admittedly difficult task, but the initiative would appear to rest with the Society, firstly because of its prestige and secondly through its diversity of membership, which already has a very wide knowledge of the requirements of the various branches of the textile trade.

Mr. S. BURGESS: It is wrong and impracticable to supply materials which are too fast and therefore too expensive; e.g. there would be no point in supplying linings and dance dresses of casement fastness to light. However, there are now a number of testing laboratories whose staffs have no practical experience of dyehouse work and who therefore set the standard of maximum fastness. If this attitude were adopted, merchants and customers would inevitably have to accept more limited ranges, flatter shades, and higher prices.

How important is fastness to wet treatment of any kind? Are complaints frequent, and is light fastness or wet fastness more important?

Mr. ROBINSON: Generally speaking, the fastness to light is of greater importance than the fastness to wet treatment. There are occasions, however, where a heavy shade is required to work against a delicate one, when a sacrifice of light fastness in order to obtain a better wet fastness of the heavy shade would be of advantage.

The number of complaints received is very small, and these refer almost entirely to defects in construction. The complaints of fading usually arise in connection with delicate shades, involving the natural yellow colour of the blend of wool used. In many instances, the supposed loss of colour is mainly an optical effect due to pile pressure having reversed the lie of the pile. Complaints of bleeding of dye are infinitesimal.

Mr. J. BOULTON: With reference to contact between producer and consumer, one of the greatest obstacles to developing an understanding of what can and what cannot be produced for given consumer needs is the correspondent in the women's column of our week-end press and in women's magazines. We are the Society of Dyers and Colourists, and it should be our job to counter publicly purveyed, half-baked ideas which in themselves are all too often an insult to our art and our profession.

Mr. A. N. WALKER*: In matters concerning dyes and their fastness this Society cannot be considered blameless, since little has been done to convey to the public a better understanding. This is a grave omission on the part of the Society. We shall be doing a great public service, and no doubt enhance the reputation of the Society, if through the

* Communicated

medium of press or radio we educate the public to a better understanding of dyes and fastness, and a committee should be formed to consider this.

There has recently been increased use of bleaching agents and optical bleaches in the manufacture of soap powders, and the publicity given by soap manufacturers to "washing whiter" implies that the washing of coloured textiles is unworthy of mention. The action of such soaps on some dyes will clearly upset the classification of fastness which the Society has so painstakingly carried out. The Society ought to protest, and the public should be told why.

Mr. G. B. Angus: There is no doubt that retailers have a difficult problem in dealing with customers' questions in respect of fastness both to light and to cleaning. The manufacturer is fully aware of the position, and every attempt is made to give the highest standards consistent with satisfying the requirements of design and colouring.

The first requirement must be to have a salable product. Shades on carpet yarn are usually produced with several dyes, and it is the constant endeavour of the manufacturers to produce shades with such a combination of dyes that the fading which takes place will be balanced, i.e. that the shades will fade on tone. It should be noted that there is no such thing as a fadeless dye. In spite of all efforts so far, it has not been found possible to use such a combination of dyes that each dye will fade by exactly the same amount under all conditions of exposure and light. Here, then, lies the cause of the trouble.

A shade which is produced with a combination of dyes to produce a balanced fade in a bright room in a sunny exposed position would not necessarily be suitable for a shady room, because of the time factor. The shade will alter after a time interval depending on the position of the carpet. If a manufacturer knew exactly where each piece of carpet made was to lie, possibly he could in the end increase the overall fastness of the carpet in each case. For general manufacture, this is clearly impossible. There can, therefore, be no clear-cut answer to Mr. Clarke's question on this score.

Similar arguments apply to the wet fastness. Requirements of the design often preclude the use of the fastest dyes in this respect, and frequently unlevel dyeing properties of the dyes themselves make it impossible to use them on yarn. Where special stress is laid on wet fastness, a customer may be asked to accept a special design in which all the shades can be produced with dyes which excel in this direction. This is already done for ships, railways, etc.

In the many cases of alleged looseness of dye to ordinary tap water which have come to my notice over the years, not one has bled with ordinary tap water spilling even when allowed to dry normally. Should the spilt liquid be alkaline, e.g. contain ammonia, then the danger of bleeding is present with heavy shades. Nevertheless, with reasonable care, the main point being to avoid overwetting the carpet, nearly all shades in carpet normally produced are quite capable of being cleaned with mildly alkaline preparations.

Thus there is no easy solution to Mr. Clarke's problems, and there are no simple answers he can give his customers.

Mr. C. O. Clark: Mr. Robinson's advice to go and examine the display of oriental rugs in one of the Harrogate shops may lead many people to form a wrong opinion regarding their original colour, for a very large proportion of the rugs imported into this country are, after arrival here, chemically washed, i.e. chlorinated, this being done not only to give lustre to the fibre but also to tone down the colours, which are often garish to our taste. This chlorination and other treatments given the rugs not only tone down the colours but often destroy them, and at one firm specialising in this process I have seen a number of girls with spray pistols busily restoring or touching up portions of the design where colours have been altered too much. This chemical washing of oriental rugs is a little-known branch of the textile industry centred in the London area, and, in pre-war days at least, it not only catered for the home market but did a large amount of processing of rugs destined for America and other markets.

Mr. A. Armitage*: A few words of explanation are necessary to avoid an injustice to a modern industry which has been established in China and to the enterprise of the world's leading dyemakers. All good-quality Chinese-made wool carpets are subjected to a very severe finishing treatment with chloride of lime and caustic soda, which the dyeings must be able to withstand. The dyemakers went to considerable expense in producing a double range of chrome and milling dyes suitable for this purpose. The above is the reason why the colouring of the Chinese carpets is comparatively dull, but they are nevertheless very readily salable. In view of the information given in the paper regarding the accepted use of fast-to-light acid dyes in the British carpet industry, we might do well to take a leaf out of someone else's book.

Mr. Robinson*: Mr. C. O. Clark was referring to the washing or lustring of Persian carpets of fairly recent origin, in order to give them an antique appearance so as to enhance their value. Such treatment alters the colourings on the surface, and makes it impossible to assess fading by a comparison with the colour of the base of the tufts.

The washing of carpets is not a new procedure, and I believe it was first carried out in a primitive manner as a safeguard against anthrax.

The Chinese specialise in the production of rugs having a distinctive finish, obtained in the manner referred to, but do not produce piece goods. I believe that the yarns are all dyed in hank by hand, in an open beck, and the dyed shades produced are by no means level, but this defect more or less disappears during the finishing operation. The dyes used must not bleed or be destroyed by the alkaline hypochlorite treatment; therefore chrome and acid milling dyes are used, together with certain acid dyes. The carpets have a backing constructed

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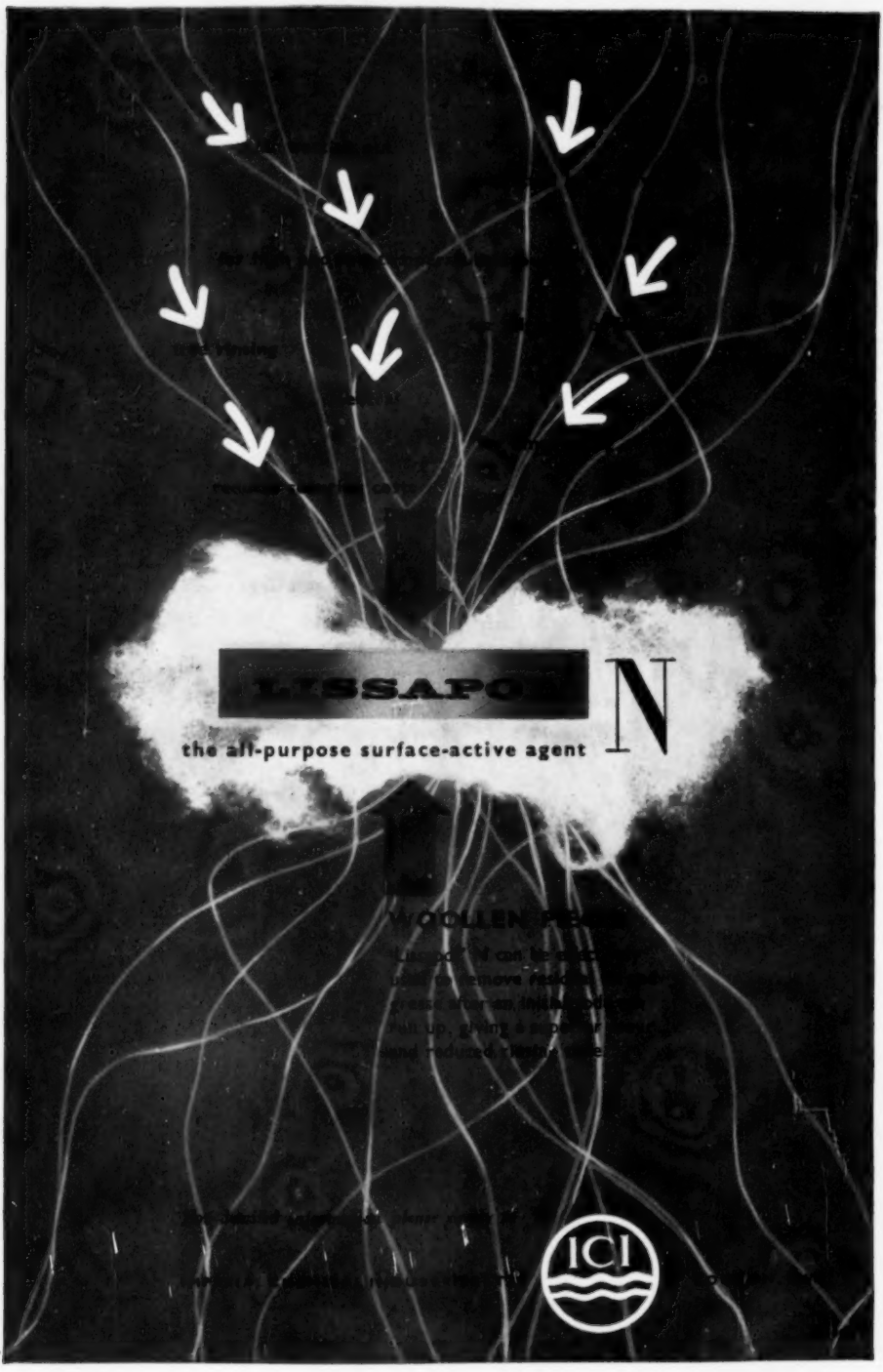
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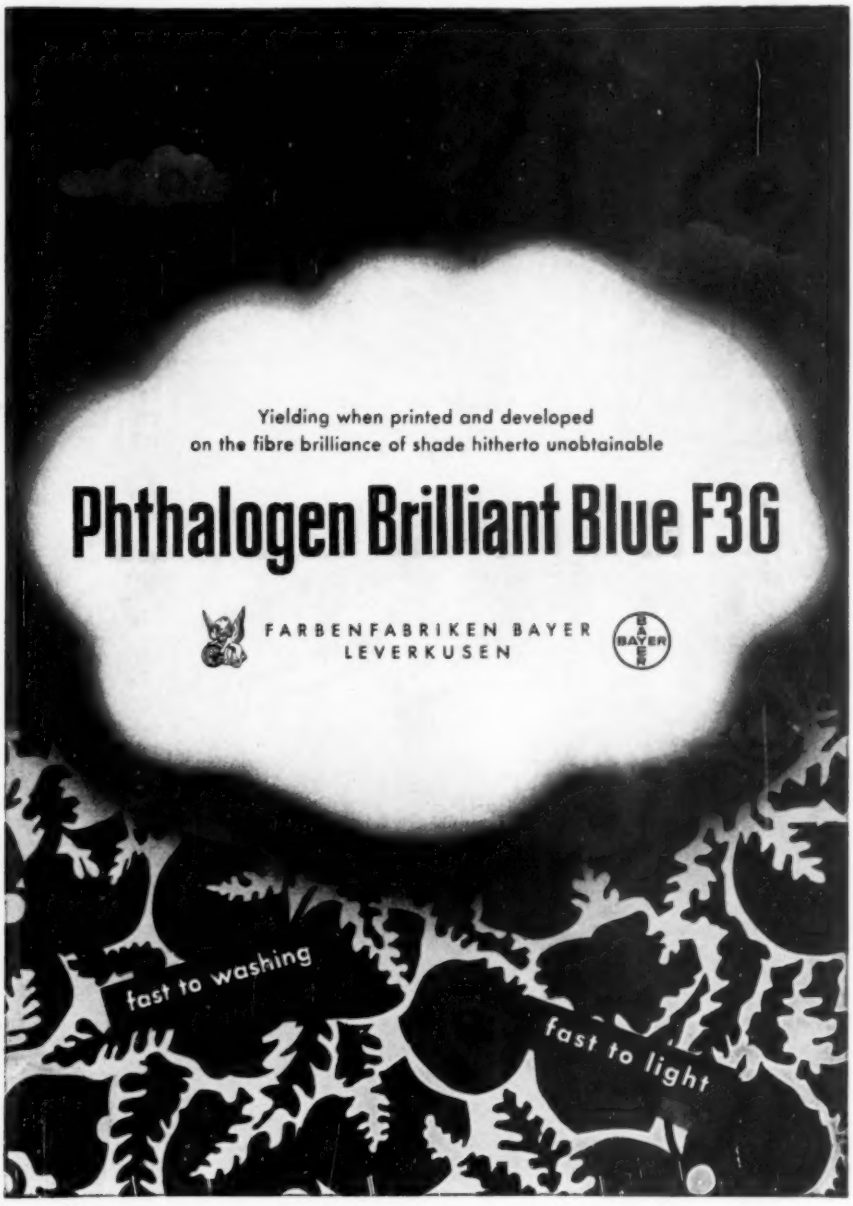
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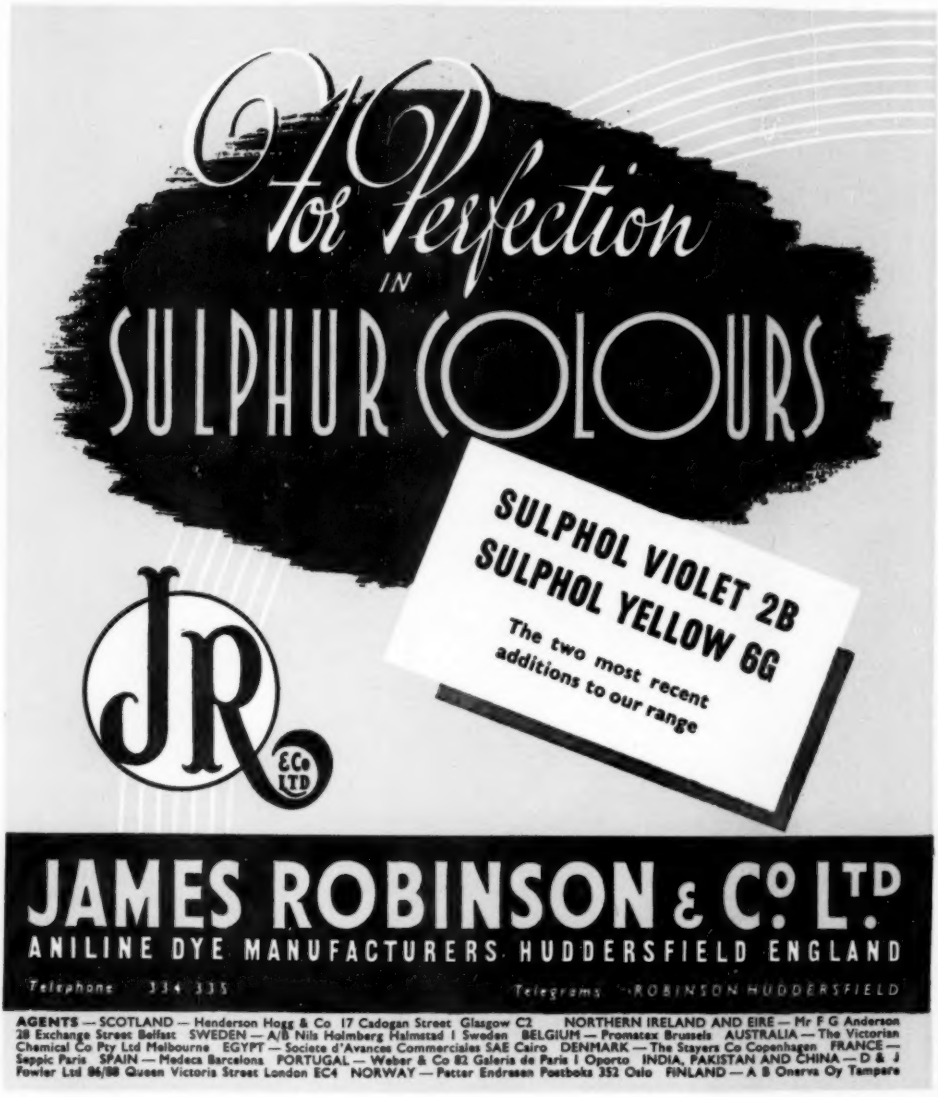
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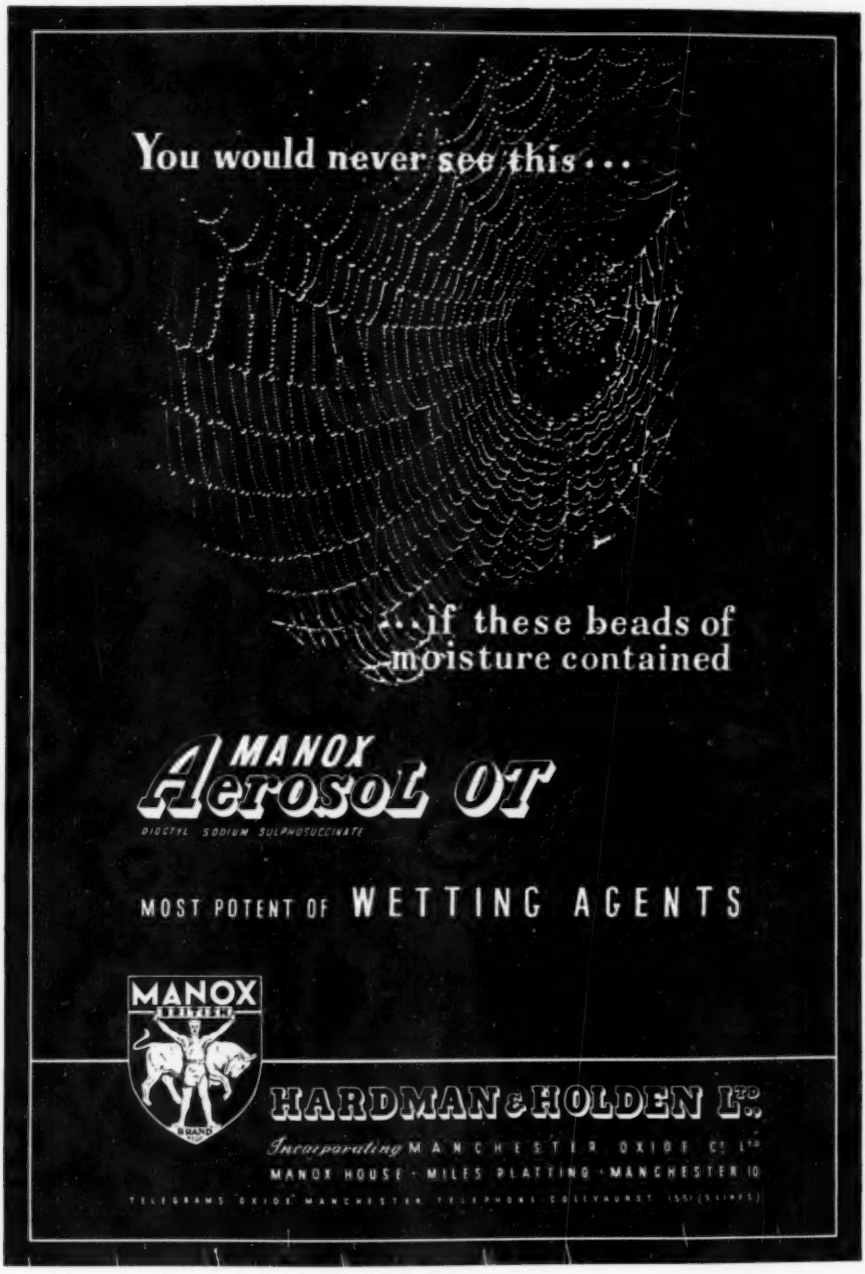
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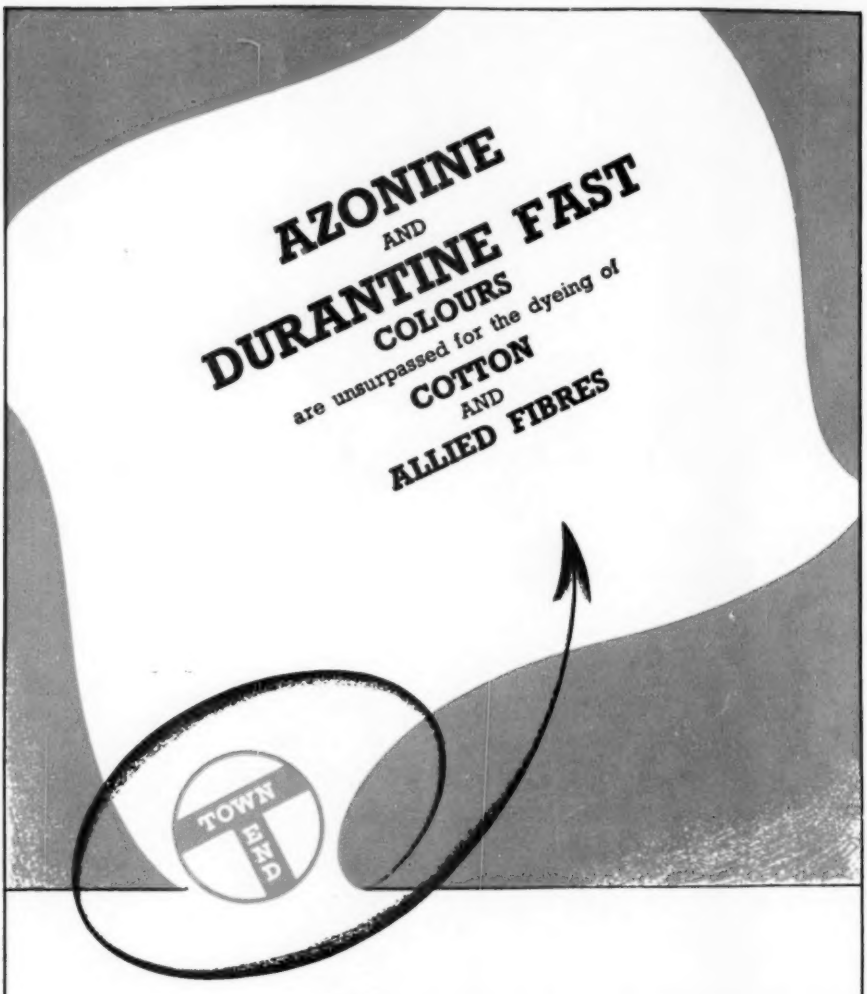


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There are firms in this country and the U.S.A. who specialise in carpet washing. Carpets have been manufactured here from yarns suitably dyed, and give satisfactory results when washed, but there does not appear to have been a demand for them.

Mr. G. E. KEY*: What is the present consumer demand for mothproof finishes, and to what extent are they now being applied in the carpet industry?

Mr. ROBINSON*: A decision with regard to the supply of mothproofed carpets rests with individual carpet manufacturers, some of whom market them whilst others supply them when requested to do so. To the best of my knowledge there is not a very great demand for mothproofed carpets either at home or abroad. In the U.S.A., where the climatic conditions favour growth of moths, the mothproofing of carpets does not appear to be the usual procedure. When selecting the method of mothproofing to be used for carpet yarns, many factors require consideration, e.g. resistance to attack by dermestid beetles or clothes' moths, permanence of the treatment, cost, guarantee by implication, and methods of testing. The report of the subcommittee appointed by the Federation of British Carpet Manufacturers to consider the mothproofing of carpets (December 1948) may be referred to for further information.

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# The Evolution of Slubbing Dyeing and Dyes

J. F. Gaunt

Development on the mechanical side of slubbing dyeing occurred mainly between 1880 and 1920, and progress during the last twenty years has been relatively slow. Slubbing dyeing is still essentially a batch operation, although a continuous process would be attractive. Although many of the dyes used for slubbing date from the nineteenth century, dyes of improved brightness and fastness are being introduced.

## Introduction

Wool is dyed in more different forms than any other natural textile fibre, and the dyeing of loose fibre, slubbing, yarn, and cloth each forms an important section of the woollen and worsted industries. The history of the dyeing of loose wool, yarn, and cloth extends over many centuries, but slubbing dyeing is of much more recent introduction. Before the extensive development of machines for carding and combing wool during the period 1830–1850, the production of combed top by hand-combing was very low by modern standards based on machine-combing, and all coloured worsted yarns were spun from wool dyed as loose fibre.

Loose-wool dyeing, followed by carding and combing, yields yarns which handle better than slubbing-dyed yarns spun from identical wool, and for this reason loose-wool-dyed worsted yarns are still not obsolete. This form of dyeing is, however, uneconomic for most types of worsted yarn, since all processes of dyeing cause some weakening and entanglement of the fibres, with the result that excessive fibre breakage occurs during carding, so that the production of noil is greater than from undyed wool. Furthermore, the noil is coloured and of less value than white noil. Dyeing carded sliver and then combing gives a superior yarn to dyeing combed top, and although the noil is coloured, only one combing operation is required as compared with two in the normal sequence of combing, dyeing, and re-combing. The former method can, however, be undertaken only by the small number of firms able to card, dye, comb, and spin within the same organisation, and as the production of worsted yarns is generally arranged on a horizontal basis, whereby combing, dyeing, and spinning are in the hands of separate firms, the dyeing of combed top is the most convenient form.

Before considering the development of machines and dyes for the dyeing of slubbing, it is desirable to outline the reasons why wool is dyed in this form—

1. Many of the most important shades of worsted yarn are mixtures of differently coloured fibres, e.g. clerical greys, consisting of black and white, natural mixtures of brown and white, and heather mixtures of three or more contrasting shades. Such yarns must obviously be dyed before spinning. Another important class of yarn comprises the marls, which consist of two or more ends, each of contrasting shade. These ends of single yarn are often solid shades in themselves, but are not strong enough to be yarn-dyed, and in any case a three- or four-ply yarn assembled from yarn-dyed singles yarn would not have the desired appearance, so that slubbing dyeing is necessary.

2. Wool dyes of good fastness to wet processing have generally poor level-dyeing properties, and consequently, where both levelness and a high standard of wet fastness are required, the wool is dyed as slubbing, so that any unlevelness can be eliminated during the thorough mixing that occurs in the various drawing operations.

Both for solid and for mixture shades spun from dyed slubbing, a very high standard of fastness to washing, and often to the even more severe processes of milling, decatising, crabbing, etc., is essential. The best possible light fastness is also required, while fastness to more specialised treatments, e.g. anti-shrink processes, bleaching, and stoving, is often demanded. On account of the high value of the fabrics ultimately produced from dyed slubbing, no risk of failure of the dye during processing or wear can be tolerated, and for this reason only dyes of the highest possible fastness are used, regardless of cost.

In the development of slubbing dyeing during the past century, progress in the design of dyeing machinery and in the production and application of dyes has proceeded concurrently, but it is convenient to consider these two aspects individually.

## I— Development of Slubbing-dyeing Machinery

In spite of the relatively short history of slubbing dyeing, there is more diversity in the types of machinery in which slubbing is dyed than with any other form in which wool is dyed. There is only one type of machine, the winch, commonly used for piece-dyeing, and at least 95% of the dyeing of woollen and worsted yarns is done on machines of the Hussong type. In the case of slubbing, however, machines designed to handle the material in two completely different forms, viz. hank and ball top, are both widely used, and there is a great number of variations on each of these principles. As one would expect, marked controversy exists on the best method of dyeing slubbing for any given purpose and also on the merits and demerits of the different types of machine. There is, however, complete agreement on the most important requirements which the machine must fulfil. It is essential that no felting of the slubbing should occur even during the most prolonged dyeing operation, as otherwise the subsequent processing is rendered much more difficult and wasteful. It is also desirable that the flow of liquor should be sufficient to ensure good penetration of the dyes through the wool, and further to enable any additions of dye made during dyeing to be uniformly distributed and not concentrated at the outer surface of the hank or ball of sliver. Ease of loading and unloading of the machine has an important bearing on the

costs of operating it, and there is considerable saving of steam and some saving of dye if a short liquor can be used. As shade requirements do not always call for batches of identical size, it is useful if the machine can be operated efficiently when not working to its normal capacity.

In an excellent review of the position of slubbing dyeing in 1937, which is incidentally the only paper on this subject published in a regular issue of the *Journal*, Isles [1] points out that the design of slubbing-dyeing machines is based on one of two principles—

(*a*) The wool is passed through the liquor.

(*b*) The wool is kept stationary and the liquor is passed through it.

The only machine operating on the former principle is the Klauder–Weldon. In a review of machines shown at the Paris Exhibition of 1889, Knecht [2] mentioned that "Klauder & Bros. of America exhibit an ingenious hank-dyeing machine". Knecht thought that this machine would be suitable for yarn, but not for slubbing, because of excessive felting, Events have proved him completely wrong in this supposition, and according to von Bergen and Mauersberger [3] after the first World War most of the slubbing dyed in America was processed on this machine. Klauder–Weldon machines of stainless steel construction are still being installed in America. In this country, the Klauder–Weldon machine was never as popular as in America, and has now been largely replaced by newer and less complicated types, but there are a few surviving examples which are held in high regard by certain dyers because of the good condition of the slubbing when the machine is carefully and skilfully operated. The difficulty of loading and unloading the slubbing, the mechanical complexity of the machine, the tendency of the slubbing to felt, and the danger of unlevelness when shading colours are added have all contributed to the decline in popularity of the machine. A good description of its construction and operation is given by Bird [4].

Machines in which the liquor is circulated through the slubbing may be classified in three groups—

1. Those in which the hanks of slubbing are suspended from poles or sticks in the dyebath.

2. Those in which the hanks or balls of slubbing are packed into a container or series of containers, through which the liquor is circulated by a pump.

3. Those in which the slubbing is mounted or is wound on to a perforated spindle, through which the liquor is forced.

### 1. DYEING SLUBBING IN HANK FORM

The earliest method of dyeing slubbing was very simple, and was identical with the process which had been in use for many centuries for dyeing hanks of yarn. The hanks were suspended from wood poles in an open vessel with smooth tops, and were turned or "broached" by means of a wooden stick similar to a billiard cue, held by two men, one at each side of the vessel. A detailed account of the technique is given by Bolton [5]. Each movement of the hanks of slubbing must have caused some felting, and the application of the natural colouring matters, most of which can be dyed only on a metallic mordant, required considerably more time than synthetic dyes. It would, therefore, be interesting to compare the amount of felting in a batch of botany slubbing dyed in an open beck by a pair of experienced labourers, using, say, camwood dyed on a chrome mordant and saddened with ferrous sulphate, with the same quality of slubbing dyed in a modern type of dyeing machine with synthetic acid or chrome dyes. In spite of the obvious disadvantages of dyeing slubbing by hand, this method was still in use on botany slubbing as late as 1910, and was considered to give very good results. As the maximum weight of the batch which could be handled by two men was only 50–100 lb., labour costs were high, and for this reason alone the method would be impracticable to-day.

The mechanisation of hank dyeing by circulating the liquor through the hanks by means of a propeller at one end of the dyeing vessel appears such an obvious step that it is rather surprising to find that the Hussong machine, which is now universally used for dyeing carpet yarn, and to a great extent for other forms of yarn and for slubbing in hank form, was introduced as recently as 1908 [6]. The original form has been modified to some extent by certain machine makers, mainly in an attempt to reduce the liquor ratio and to give a more even flow, but does not differ greatly from the present pattern. The Hussong machine has for many years been an important machine for dyeing all qualities of slubbing other than French combed top, which tends to break under its own weight when wet, on account of the relatively short fibre length. The machine corresponding to the Hussong on the Continent is the Esser, in which the hanks are supported by sticks at both top and bottom, and consequently they have less freedom of movement when the liquor is circulated in an upward direction, but this type is not used to any appreciable extent for slubbing.

### 2. DYEING SLUBBING IN CONTAINERS

Throughout the history of slubbing dyeing, there has been a succession of different types of machine to dye hanks or balls of top by passing the dye liquor through them. One of the first attempts was made before 1885 by the firm of Dreze in Verviers, who employed a machine similar in principle to the Simplex, the liquor being distributed over the hanks or balls of top from a central vomiting pipe. This machine was not fitted with an air injector, and consequently the liquor could be circulated only at the boil. It is now quite obsolete, no doubt owing to the poor condition of the slubbing after being in contact with the violently circulated boiling liquor.

The early issues of the *Journal* give several interesting sidelights on the development of top-dyeing machines from 1884 onwards. The first reference is an abstract of a patent [7] granted to Titus Salt and William Stead for "Improvements in Apparatus for Washing, Scouring, Dyeing

Fibrous Materials in the Form of Slivers, Slubbings, etc.". This was an early form of machine for treating and dyeing slubbing in ball form, and appears similar in principle to machines still in use, but no further reference to it can be found.

Probably the oldest design of the top-dyeing machines still in regular large-scale use is the Calvert Jumbo, which is used also for dyeing loose wool. This machine dates from about 1880, and by 1907 at least fifty of the machines, ranging in capacity from 150 to 700 lb., were in operation. This machine is popular because of its simplicity of design and ease of operation, although care is needed in selecting shading dyes of good penetrating properties. Slubbing is dyed either in the form of hanks packed evenly on the false bottom, or as balls of top with the interstices filled in with slubbing unwound from other balls.

In his account of dyeing machines at the Paris Exhibition, Knecht [2] mentioned also a copper Obermaier machine for dyeing slubbing in the ball, and said that "this machine appears to have met with great success on the Continent". In this machine, which was first produced in this country in 1886, although it had been used at an earlier date on the Continent, the balls of slubbing were packed in the annular space between a perforated central tube and a perforated outer cylinder, to which the inner tube was attached by the base plate. The cylinder fitted into the dyeing vessel, but was removable for loading and unloading the tops, and the liquor was circulated through the tops from the inside of the cylinder by means of a pump. Uniform packing of the tops was essential to prevent channelling and unlevel dyeing. This type of machine was later manufactured by other firms of machine makers, and versions of it are still in regular use by several firms in the West Riding. The Geisler machine operated on a similar principle, but was fed from an overhead reserve tank into which the liquor was pumped, thereby giving a constant head.

Between 1890 and 1895, Obermaier followed this early type with the machine known colloquially as the "Revolver", in which the large perforated cylinder was replaced by a central tube to which small cylindrical receptacles, each holding one or two tops, were attached horizontally in staggered rows. As in the earlier machine, the liquor was circulated by pump through the tops from the hollow central tube and through the perforated lids of the cans. The great disadvantage of this machine was that the tops tended to collapse in the cans when the liquor was run off and replaced by a fresh liquor, as was necessary for chroming many dyes, or if the dyebath had to be cooled in order to make an addition to the dyebath. In spite of all attempts to rearrange the tops within the cans, it was usually impossible to prevent severe "channelling", as the liquor preferred to travel through the space above the top rather than through the top itself, and consequently very unlevel results were occasionally produced. With the advent of later and improved dyeing machines, this type is now practically obsolete, as is the Keukelaere machine, in which the tops were dyed in horizontal cans similar to those of the "Revolver", but fixed to a narrow hollow rectangular chamber instead of the central hollow tube of the Obermaier machine.

The only important type of machine now used for dyeing balls of top in separate containers is the C.D.B.* Patent Top Dyeing Machine, which was first produced in 1917. In this machine, the cylinders are vertical, and consequently any decrease in volume of the tops during dyeing does not affect the cross-sectional area. The danger of channelling mentioned above in the case of the Obermaier machine is thereby eliminated. Other advantages of the C.D.B. over the Obermaier type are the greater ease of unloading of the dyed tops, as if the lids of the cans are removed after dyeing and the pump is started for a few seconds, the tops are gently pushed out and are easily removed by hand; while the capacity of the machine is much more flexible than that of all other types in that cylinders can be left empty if required, without impairing the circulation of the other cans, by turning a valve in the base of the cans.

Whereas the dye liquor is circulated parallel to the axis of the ball of top in the last three types of machine, in the Triumph machine the tops are placed on their sides in horizontal trough containers and covered with detachable perforated lids, the liquor passing through the top vertically to the axis. This machine, which was invented by G. Wordsworth about 1923, works on a lower pressure than other forms of can dyeing machine, and for this reason is claimed to preserve the handle of the wool. It is also more tolerant of variation in the size of the top than are other top-dyeing machines.

### 3. DYEING SLUBBING ON PERFORATED SPINDLES

The Abbott machine, which is widely used in America, is the only machine now in use for dyeing slubbing wound on to perforated spindles, through which the liquor is circulated from a pump. A number of advantages are claimed for the machine—e.g. simplicity of drying as compared with the methods required for drying slubbing dyed in the machines described above, and the condition of the slubbing is said to be preserved during dyeing, but the Abbott machine is practically unknown in this country. A full account of the machine is given by von Bergen and Mauersberger [3]. It may be mentioned that between 1905 and 1910 there were a few machines in the West Riding in which tops were dyed on vertical perforated spindles connected to a pump as in the Abbott machine. The middle of the tops was pulled out by hand to form a hole through which the spindle passed, four or five tops being fitted on each spindle and clamped down through a metal plate at the upper extremity. The parts of top removed in this way were gilled together and wound into balls of top, which were then used to make up the load. This type is no longer used, as the condition of the sliver compared unfavourably with that produced in other machines.

* Callebaut-de Blicquy

### PRESENT POSITION OF SLUBBING-DYEING MACHINERY

The worsted spinning trade produces yarn for two main classes of trade—(*a*) weaving and (*b*) hosiery. Each of these has different requirements: the ideal weaving yarn would be quite unsuitable for knitting, and *vice versa*. The former requires to be a smooth yarn with relatively high twist, so that the finished cloth has a clearly defined pattern, free from the blurring that would arise from loose fibres protruding any appreciable distance from the yarn; but a hosiery yarn requires to have the maximum bulk and softness, and no dyeing process can be tolerated which would interfere with this. The machine employed for dyeing the slubbing has a considerable bearing on the properties of the finished yarn, and in view of the varied requirements of the latter no single type of machine can be regarded as the best for all purposes. A number of factors, not least the personal preference of the dyehouse manager, have to be taken into consideration.

Comparative trials of slubbing dyeing in a top-dyeing machine and in a Hussong machine respectively have shown that the product from the latter is loftier than from the former, in which the pressure of the liquor during dyeing causes some setting of the fibres. It has been found within the past two or three years that the pressure of 8–10 lb. per sq. in., formerly considered essential for circulating the liquor in a top-dyeing machine, can be reduced to 3–4 lb./sq. in., and this has led to less compression of the dyed slubbing, with a consequent improvement in the loftiness of the resultant yarn.

As greater variation in shade can be tolerated in slubbing, which is thoroughly mixed before spinning, than in the case of yarn or piece, in which no further mixing is possible, it might have been expected that continuous dyeing would be widely employed, possibly on the lines of the Standfast process [8] or of the method suggested by Casty and Krähenbühl [9]. This is not the case, probably because the rate of strike of acid and chrome dyes on wool is much lower than that of leuco vat dyes on cellulosic fibres, while the chroming of mordant dyes on wool by any of the existing processes is too slow to allow either of the above methods to be used for applying chrome dyes to wool.

To summarise, therefore, no outstanding advance in slubbing-dyeing machines has occurred for at least twenty-five years. Many improvements in detail have been made, however, and the use of stainless steel is now almost universal for the construction of new machines.

### DRYING SLUBBING

The drying of dyed sliver is one of the less satisfactory aspects of slubbing dyeing. There are two main drying methods in use in this country—

(*a*) Hank drying in a hot-air chamber

(*b*) Sliver drying over heated metal cylinders.

The former method is invariably used when the slubbing has been dyed in hank form. The hanks are first hydroextracted, and are then dried over poles in the type of machine used for drying hanks of yarn. The disadvantage of the method is the difficulty of converting the hanks into a form suitable for the machines on which the slubbing is next processed. As hanks cannot be fed direct to a gill-box or comb, it is necessary first to place the hanks by hand on to a "top hat", which is a metal shape mounted on a vertical spindle, and from this they can be led through rollers into cans or on to a balling head.

Slubbing is usually dried in a backwashing machine when it has been dyed in ball top. The need for backwashing is much less with modern dyes than when dyewoods were used, as there is less danger of colour adhering loosely to the surface of the wool, and for this reason the washbowls of the backwash are sometimes left empty, the dyed and hydroextracted tops being led direct on to the heated cylinders, and then on to the gill box and balling head. The drying of tops in this way calls for much less handling than after drying in hank, but it is considered by many dyers that drying under tension in close contact with heated cylinders causes some setting of the fibres and leads to a less lofty yarn. The rate of transfer of heat from the cylinders and hot air to the wet slubbing is rather low, and it is not easy to dry slivers retaining more water than the normal type of wool top, e.g. mixtures containing cellulosic fibres. As shown in Table I, the moisture remaining after hydroextraction in slubbing consisting of mixtures of wool with other fibres varies considerably. All these figures relate to 50 : 50 mixtures of 64s wool with other fibres in staple form; all the slivers were hydroextracted together after dyeing, and the figure for excess water represents the amount calculated on the weight at correct condition.

TABLE I

| Type of Slubbing | Excess Moisture (%) |
|---|---|
| 64s Wool ... ... ... ... | 31·2 |
| Wool–nylon ... ... ... ... | 20·2 |
| Wool–Thermovyl ... ... ... | 22·5 |
| Wool–Fibro ... ... ... ... | 57·3 |
| Wool–Celafibre ... ... ... | 28·6 |

The spools of slubbing on the spindles of the Abbott machines are not hydroextracted after dyeing, but are transferred direct to a special drier, in which hot air is blown through the spindles. This method is claimed to be very effective, and handling is reduced to a minimum, but the amount of water present in the slubbing at the commencement of drying and requiring to be evaporated must be considerably greater than in the methods described earlier.

Methods of drying tops by infra-red or radio-frequency methods have been considered, as they would enable balls of top to be dried directly after hydroextracting without further disturbance, but as pointed out by Thomas [10], such methods are at present uneconomic on account of power costs.

## II—Development of Dyes for Slubbing

The discovery of the first synthetic dye by Perkin in 1856 coincided with the rapid development of machine-combing, and therefore of slubbing dyeing, but it was many years before synthetic

colouring matters were used to any extent on slubbing. Rowe [11] mentions that Perkin visited Bradford in 1858 to show dyers how to apply Mauve to wool, and it is probable that slubbing dyers were attracted by the brightness of other early basic dyes, e.g. Magenta (1859), Methyl Violet (1861), and Malachite Green (1877), in spite of their lack of fastness. Such dyes, although of interest as novelties, were not used for producing blacks, browns, navies, maroons, and bottles, which were then, as now, the backbone of all ranges of slubbing-dyed shades. All these shades were obtained with natural colouring matters for many years, until synthetic dyes possessing superior dyeing and fastness properties became available. Thus, blacks were based on logwood, browns on mixtures of fustic, madder and logwood, navies on indigo, maroons on madder or synthetic alizarin, first made available in 1869, and greens on indigo topped with fustic. With the exception of indigo, all these were dyed on wool mordanted with chrome and/or aluminium, copper, iron, or tin salts, while before the invention of the hydrosulphite vat in 1871 indigo was invariably dyed from a fermentation vat.

Although the natural colouring matters gave a richness of shade which in most cases cannot be obtained in any other way, they were rapidly displaced for slubbing dyeing by the remarkable development of acid and chrome dyes between 1890 and 1905, largely because of the lengthy dyeing process involved and the inferior fastness to light of such dyeings as logwood and fustic, while the rubbing fastness of many of the blacks and navies was extremely bad by modern standards. The growing popularity and importance of synthetic dyes can be traced in the *Journal* of 1888 onwards. In a series of papers on new dyes, Knecht reported the introduction of Patent Blue [12] and Alizarine Green SW [13], while by 1894 it was clear that the new alizarin dyes, especially the blues, were gaining ground, and that Mordant Yellow and Anthracene Yellow were replacing fustic [14]. By the turn of the century, synthetic dyes were firmly established for slubbing dyeing; many of the dyes and practically all the dyeing methods still regularly employed by modern slubbing dyers were in current use; while the presence of even small amounts of iron and copper in the dyebath was beginning to be regarded as an unmitigated nuisance—a view heartily shared by modern slubbing dyers!—and not as an essential part of the dyer's craft.

In order to survey the progress in wool dyes during the past fifty years, it is convenient to consider them under the following three headings—

1. Chrome dyes
2. Acid dyes
3. Other types.

### 1. CHROME DYES

Of the chrome dyes used in large weights by present-day slubbing dyers almost every one was widely used by 1914. The dates of discovery are shown in Table II, most of the details of which have been taken from Rowe's monograph [11]. Each of these dyes is now made by several manufacturers and marketed under a variety of names.

TABLE II

| | |
|---|---|
| Eriochrome Black T ... ... ... | 1904 |
| Diamond Blacks PV and P2B ... | 1902 |
| Alizarine Blue Black B ... ... | 1894 |
| Eriochrome Blue Black R ... ... | 1904 |
| Eriochrome Azurole B ... ... ... | 1906 |
| Metachrome Browns B and R ... ... | 1898 |
| Palatine Chrome Brown 2G (Brown RH) | 1911 |
| Anthracene Chrome Brown EB ... | 1906 |
| Eriochrome Red B ... ... ... | 1904 |
| Alizarine Red S ... ... ... | 1871 |
| Acid Alizarine Red B ... ... ... | 1902 |
| Anthracene Yellow C ... ... ... | 1891 |
| Eriochrome Verdone ... ... ... | 1907 |

Slubbing dyers have their individual preferences for different members of the above list. Thus, many dyers prefer Diamond Black PV to Eriochrome Black T, in spite of its higher cost and slightly greater difficulty of application, because it is free from the danger of staining adjacent white wool if allowed to stand wet. Similarly, all three browns mentioned in Table II are used for slubbing, Brown RH having a much more attractive shade than Metachrome Browns B and R although it is much more expensive, whereas Brown EB has extremely good fastness to milling, carbonising, and acid cross-dyeing. These and many similar cases must be considered on their own merits in the light of local conditions.

Although hundreds of tons of each of the above dyes have been used during the past forty years, this is not because no improvement in properties is desirable. For example, a navy blue dye similar to Eriochrome Blue Black R, but slightly brighter in shade, would render unnecessary the customary addition of the fugitive and expensive Eriochrome Azurole and Naphthachrome Violet. This need was met to some extent by Metachrome Brilliant Blue BL, but this dye is much too expensive for general use in navies. Similarly, an improvement in the light fastness of Eriochrome Red B would enable it to be used with safety in pale shades, and this is also the case with the three chrome browns mentioned above.

All the dyes in Table II marked an improvement over the dyes previously used in that they are all (with the exception of Metachrome Brown B and Alizarine Blue Black B) best applied by the after-chrome process instead of the slower chrome mordant method. This was not an unmixed blessing, however, as it rendered obsolete such dyes as Alizarine Blue WR, Gallocyanine, and the Alizarine Cyanines, the shades of which are impossible to reproduce in other ways. In the search for new chrome dyes of improved shade and fastness properties, there appears to have been an obsession with good metachrome dyeing properties, and with the exception of the Naphthachrome Violets and Chromoxane Brilliant Red BL there have been few new dyes not specifically designed for metachrome dyeing. No slubbing dyer would deny the virtues of the excellent ranges of metachrome dyes, the members of which are selected for good level-dyeing properties and compatibility in

dyeing, for balanced fading on prolonged exposure to light, and for general all-round wet fastness. They are particularly suitable for pale and medium shades, but in greater depths they often prove extremely expensive and do not show very great advantage over the older dyes. To obtain a dye possessing good metachrome dyeing properties, it is often necessary to use expensive intermediates, and it would be illuminating to learn how many good and inexpensive dyes of otherwise desirable properties have been sacrified on the altar of high metachrome efficiency.

To sum up, heavy shades are produced with chrome dyes and dyeing processes practically identical with those in use forty years ago, but for pale shades a very fine range of metachrome-dyeing dyes is widely used. The chrome mordant process is now obsolete. A considerable amount of research work on the theoretical aspects of dyeing with chrome dyes has given very useful practical results. The work of Lister [15] on the relationship between dyeing properties and dyebath pH has been of considerable assistance in selecting suitable mixtures of chrome dyes. Peryman [16] has pointed out that the pH of a metachrome dyebath may rise to an undesirably high level, but the saving in time and the fastness properties of the best metachrome dyes more than compensate for the somewhat greater amount of noil produced during the combing or recombing of sliver dyed by this process as compared with similar material dyed at a lower pH. Another interesting point recently discovered is that the oil content of dyed slubbing is practically unaffected even when dyed by the afterchrome process [17], as it had hitherto been considered that a considerable proportion of the oil passed into the dyebath.

### 2. FAST ACID DYES

Acid dyes have been used for many years to supplement the rather dull range of shades obtained with chrome dyes, and most of the early acid dyes were dyed on slubbing. Standards of wet fastness in the nineteenth century must have been considerably lower than those now insisted upon, for as late as 1901 the Badische Anilin- und Soda-Fabrik in their magnificent pattern card [18] recommended such dyes as Tartrazine, Orange II, and Wool Green S for slubbing dyeing. At that time, several dyes still widely used for slubbing dyeing, such as Alizarine Cyanine Green G and Anthraquinone Violet, which date from 1894 and 1898 respectively, were available, as were many more which have had a long career but are now being replaced by faster dyes, such as Alizarine Sky Blue B (1899), Cyananthrol R (1908), Fast Acid Violet 10B (1891), and Sulphon Cyanine GR (1892).

The history of the fast acid dyes is very different from that of the chrome dyes outlined above, as very few of the dyes now in regular use were available fifty years ago, and even the two examples mentioned in the last paragraph are now obsolescent with the advent of new products. Progress has been steady, rather than spectacular, and for that reason is best appreciated by comparison of the most recent editions of the dyemakers' pattern cards with their counterparts of fifteen or twenty years ago. The last fifty years have seen rapid development, particularly in the azo and anthraquinone series, as a result of which a range of fast and bright shades is now available which must have been beyond the dreams of the dyer of a century ago.

There are now few shades which cannot be produced so that they withstand milling or repeated washing, and with a light fastness of at least 5 on the S.D.C. scale [19]; in some cases, particularly fawns and greys, a much higher standard of light fastness can be obtained. The only worries which the slubbing dyer feels on the score of lack of fastness are a few very bright shades, the most important of which are peach and pink. There is no vat, acid, or chrome dye of good fastness to light and washing, even when dyed in presence of a fluorescent whitening agent, which approaches the brightness of the basic Rhodamines, and particularly that of the Sulpho Rhodamines B and G. Baby pink and peach shades are very important on hosiery and hand-knitting yarns, in which case brightness is demanded even at the expense of fastness, and the discovery of a fast, bright pink is anxiously awaited by all slubbing dyers. Other shades where some improvement in fastness is required are bright greens, which have to be dyed with Brilliant Indocyanine G and Milling Yellow H5G, and bright greenish blues similar to Patent Blue A.

The general object in producing new fast acid dyes is to combine the fastness of chrome dyes with the brightness of level-dyeing acid dyes. This is well illustrated by the Carbolan (ICI) range; e.g. Carbolan Yellow 4GS has a similar shade to Xylene Light Yellow 2G but very much better wet fastness. Many new dyes have properties similar in many ways to well proved existing types, but without the deficiencies of the latter; e.g. Supranol Scarlet FGN has a similar shade to Polar Red G, and is comparable in wet fastness, but is free from the sensitivity to sulphur dioxide, which turns the latter dye yellowish orange.

Although the range of fast acid dyes now available to the slubbing dyer is a great advance on that of even twenty-five years ago, there is every reason to believe that new dyes of increased brightness, better fastness to light and wet processing, and greater ease of application will continue to appear at their present rate.

### 3. OTHER TYPES

Before the development of fast acid dyes, direct cotton dyes were used to a considerable extent for bright shades where good washing fastness was required. Chrysophenine was particularly important for slubbing dyeing from 1900 until about 1910, because of its good fastness to light and washing, its attractive shade, and its good metachrome dyeing properties. The only cotton dye now used on wool is Benzo Fast Red F, and this is of more importance for loose wool than slubbing.

Premetallised dyes of the Neolan (Ciba) type have been of interest to slubbing dyers since they first appeared in 1912, especially for mode shades such as fawns, silvers, and greys, in which they have excellent fastness to light and washing. It is usual to apply them from a bath containing either

ammonium sulphate or a small amount of sulphuric acid, and not from the conventional strongly acid dyebath, because of the adverse effect of the latter on the properties of the wool. The good levelling properties of this class of dye are not seen to best advantage in this way, but the levelling is adequate and the exhaustion is very good. As the shades of the premetallised dyes can be produced with at least equal fastness with chrome or acid dyes, and as advantage cannot be taken of their migration properties, these dyes are of much less importance on slubbing than on cloth or yarn.

Indigo was used almost exclusively for producing blues on slubbing prior to the discovery of chrome and acid dyes of good fastness, and is still employed on blues for Admiralty contracts and as the coloured component of military grey half-hose. Its fastness to light and wet treatment is unsurpassed by any other dye, but it is difficult to apply to slubbing, even in hank form, and its rubbing fastness often leaves much to be desired. Many dyers prefer to obtain indigo shades with Indigosol O (DH) or Soledon Indigo LLS (ICI), the dyeing method of which is much more similar to that of an acid dye, or alternatively the wool is sometimes dyed as loose wool with indigo, as the fibres are much less impaired by vat dyeing at relatively low temperatures than by dyeing at the boil with other types of dye. Although the wet fastness of vat dyes on wool is better than can be obtained with any fast acid dye or most of the chrome dyes, they are used on slubbing only for special purposes, e.g. when absolute fastness to decatising or peroxide bleaching in admixture with white wool is required, because of the difficulty of application, and particularly of matching the desired shade. Furthermore, the light fastness of the thioindigoid types is not very good, while most of the anthraquinone vat dyes require too strongly alkaline a vat for wool, and attempts to dye them from less alkaline vats, e.g. in presence of trisodium phosphate, give poor exhaustion. The solubilised vat dyes of the Indigosol (DH) and Soledon (ICI) ranges are not used to any extent on wool, mainly because of the difficulty of developing them. It is to be hoped that some simple method of overcoming this difficulty will be found, as the fastness properties of many of these dyes, especially in bright pastel shades, are better than can be obtained in any other way.

## Future Prospects of Slubbing Dyeing

It is exceedingly difficult to attempt to prophesy the future development of slubbing dyeing. There seems little likelihood of any other form of dyeing being used for multicoloured worsted yarns consisting entirely of wool, but in view of the length of time for which a large amount of capital is tied up while coloured tops are being converted into yarn, and the attractiveness of holding a stock of undyed yarn which can be dyed as required, there is every incentive to devise alternative methods of dyeing, at a later stage of processing. Thus, although there is a growing demand for a high standard of washing fastness on hosiery yarns, many of which were formerly dyed with level-dyeing dyes the washing fastness of which was particularly unsatisfactory after anti-shrink treatment, this is being met to a large extent by improved techniques in yarn dyeing and not by slubbing dyeing, as would formerly have been the case. The experience gained in this way will, therefore, probably lead to a reduction in the amount of slubbing required to be dyed for solid shades. Attractive mixture effects can be obtained by dyeing yarn or piece consisting of mixtures of wool with regenerated cellulosic and synthetic fibres, and the use of these fibres mass-dyed prior to extrusion is particularly interesting. One can confidently expect further developments along these lines, which will lead to effects similar to those hitherto obtainable only by slubbing dyeing. The extent to which such materials will finally be adopted obviously depends to a greater extent on economic, rather than technical, considerations.

It has already been mentioned that slubbing dyeing is a process which should lend itself to continuous treatment, but that it is still exclusively a batch operation. In view of the lack of progress on the mechanical side of slubbing dyeing for the past twenty-five years, research on this aspect is overdue. Steady development of fast dyes for slubbing has proceeded for many years, and the gaps in the various ranges are well appreciated by all concerned, so that new and improved dyes and dyeing techniques can be anticipated.

* * *

The author thanks the Directors of Patons & Baldwins Ltd. for permission to publish this paper. He also acknowledges the assistance given by Mr. F. H. Marsh and Mr. C. Callebaut of the Longclose Engineering Co. Ltd., by Mr. J. F. Pell of the J. Farrar Engineering Co. Ltd., by Mr. C. P. Atkinson of Mather & Platt Ltd., and by Mr. J. D. J. Elliott of Calvert & Co. Ltd.

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## Discussion

Dr. GAUNT: Controversy on the various methods of slubbing dyeing is inevitable because of the different end-uses of slubbing-dyed worsted yarns. Thus, in a comparative examination of slubbing dyed in Hussong and Longclose machines, the former gave a bulkier and loftier yarn, which from the point of view of the hosiery trade was an advantage, although this would not necessarily be the case in a yarn for the coating trade. Similarly, drying slubbing over heated cylinders in a backwash leads to a less lofty yarn than drying in hank form, presumably owing to some slight setting of the fibres under tension. Nevertheless, many slubbing dyers use Hussong machines for the coating trade and Longclose for the hosiery trade, both with very satisfactory results, and both methods of drying are used for all types of slubbing, so that it cannot be said that there is any *best* method of dyeing or drying slubbing.

Critical reviews of dyes would be an interesting and very useful innovation for the *Journal*—such reviews appeared several times about sixty years ago.

The major improvements in dyes during the past 50–60 years have been in fastness and ease of application. However, current trends towards extending the range of metachrome dyes have been exaggerated, and have resulted in a number of very expensive dyes, whose cost is several times that of older afterchrome dyes, which were but little deficient in fastness properties and might even be faster to certain wet processes. Furthermore, the effect of metachrome dyeing on wool is under considerable suspicion, although final proof is lacking.

Further research is desirable by the dyemakers into the production of a bright pink dye possessing improved light fastness. Within the past few years, the light fastness of fluorescent whitening agents has been very much improved. Information gained in this way might enable improvements to be made in the bright fluorescent type of dye.

Mr. W. A. EDWARDS: While loftiness is a valuable feature in hosiery yarns, it must be noted that for certain types of hosiery, e.g. footwear, stability is also a very important requirement.

Slubbing dyers should appreciate the importance to the hosiery industry of the use of excessive amounts of topping colour, which may cause serious trouble in scouring and shrink-resist processing. For example, in military grey half-hose, where a blue or violet topping colour may have been used, this may be liable to bleed into the white in the mixture during processing, and the fault may be wrongly attributed to the hosiery finisher.

Dr. GAUNT: No self-respecting slubbing dyer would use excessive amounts of shading colour. For military grey half-hose my own firm use only Indigo as the blue component, as laid down in the specification.

Mr. A. H. KNIGHT: The author has quoted 7d./lb. as the dyeing expense for metachrome dyes compared with 1d./lb. for afterchrome dyes. Does this order of cost difference apply throughout the shade range?

Dr. GAUNT: The cost ratio of 7 : 1 holds for many shades, but is by no means universal. Do not many of the new metachrome dyes contain expensive intermediates purely for the sake of good metachrome dyeing properties rather than improved light or wet fastness?

Mr. KNIGHT: It is true that special constitutions have had to be devised for metachrome dyes, often entailing the use of more expensive intermediates than at present go into the making of commercial afterchrome dyes. The one-bath technique has been developed, however, to make the user's application of chromable dyes simpler from the operational point of view.

Dr. G. H. LISTER: The lecturer has cast a shadow over an extremely important dyeing method. In the written text he states with some certainty that metachrome dyed slubbing produces more noils and fibre breakage than other dyeing methods. From the platform, however, he admits that the matter is still *sub judice*.

It would be of interest to know whether Dr. Gaunt's data relating to the high noil content were obtained from experiments carried out before the appearance of Peryman's letter [16]. Peryman undoubtedly did a great service in calling attention to the high pH which could develop during metachrome dyeing if ammonia was unable to escape from the dyebath. As far as I am aware, however, conditions now are adjusted so that such high pH values do not develop, since they are not an essential requirement for a good metachrome dyeing. Under controlled conditions of pH the noil and fibre breakage is probably no greater than by the afterchrome process.

Other dyeing methods also give rise to high pH values, e.g. with so-called neutral-dyeing acid dyes, and it is possible that under such circumstances fibre breakage will be higher even than in the uncontrolled metachrome process, since there is no possibility of chromium forming new cross-links at broken cystine bonds.

Many of the modern metachrome dyes possess also excellent fastness to light and wet treatments, and in this respect are often far superior to the older afterchrome dyes. At the same time the fact that a dye is not precipitated in solution by chromium automatically brings with it two virtues which are not possessed by non-metachrome dyes, firstly the ability to salt, and secondly a possibility of better application to yarn, even if the afterchrome process is used. Many of the difficulties of yarn dyeing arise from the mechanical faults of the machine. One of the complications is that, at the moment of adding the chrome, when the dyebath is considered to be sufficiently exhausted, the lake is immediately formed, and is precipitated on the outside of the material. If, however, the dye has metachrome dyeing properties, there is less likelihood of this taking place. Therefore, research on metachrome dyeing properties may be justified in that the demand for fast shades on yarn is more likely to be satisfied by dyes with metachrome dyeing properties.

Dr. GAUNT: It is well known that there is a great need of a single reliable method for estimating damage and degradation in wool fibres. However, from careful records kept over a considerable period and relating to many hundreds of thousands of pounds of carded sliver of a wide range of qualities, my colleague Mr. H. V. Dyson has conclusively shown that the amount of noil produced by sliver dyed by the orthodox metachrome process is greater than that produced by other processes. The suggestion that dyeing with acid dyes in a neutral bath may cause greater fibre damage than dyeing by the metachrome process does not take into account the fact that alkali is liberated in metachrome dyeing. To describe the uptake of chromium as simply as possible, removal of chromic acid by the wool leaves its chemical equivalent of sodium hydroxide in the bath, and Peryman has shown that the evolution of ammonia by reaction of this alkali with the ammonium sulphate is by no means complete during the usual dyeing process.

While precipitation by chromium in the dyebath does occur with a few dyes, e.g. Eriochrome Black T (Gy), a much larger number of chrome dyes are unsuitable for use by the metachrome process because of their poor affinity for wool from a neutral bath. Many of these dyes, e.g. Acid Chrome Blue 2R (IG) and Solochrome Flavine RS (ICI), have levelling properties of a very high order when applied from an acid dyebath, and are at least as satisfactory for yarn dyeing when applied by the afterchrome process as newer metachrome dyes dyed by their own method. As no research to produce level-dyeing afterchrome dyes of this type appears to have taken place for many years, work in this field by dyemakers is overdue.

Mr. H. FOSTER: The lecturer's statement that yarns spun from Hussong-dyed slubbing were more lofty than those from can-dyed slubbing is in accordance with results shown to me before the war. These results are somewhat analogous to piece finishing: if a firm piece is wanted, it is given some "set", i.e. hot wet treatment whilst the fibre is held. This is what occurs in can dyeing, particularly with the top in ball form. Photomicrographs would probably show that can-dyed slubbing has acquired some set.

Mr. C. O. CLARK: It is very doubtful whether fibre breakage is a true indication of how wool will behave in wear. Thus the German army insisted on their wool being vat-dyed on the grounds that there was less fibre breakage in carding than if it were chrome-dyed, and inferred from this that not only did vat dyeing result in a better yield of cloth from the raw wool but that the garments made from such cloth would wear longer. The S.S. carried out large-scale trials involving thousands of men and showed that, although it was true that vat-dyed wool broke less during carding than chrome-dyed wool, yet garments made from the latter wool wore much better than those from the former, so much so that the increased life of the garments more than compensated for the wastage due to fibre breakage in carding. Thus the wool which fibre breakage would appear to indicate as being the weaker is, from the viewpoints of both the ultimate consumer and the national economy, the stronger.

Mr. A. WHITEHEAD*: The German Air Force preferred to have their uniforms made with wool dyed with chrome dyes. It would appear, therefore, that the authorities in Germany were divided in their opinions as to the best method of dyeing wool for uniforms.

Mr. S. BURGESS: It is difficult to see who would now undertake critical reviews of dyes on the lines of those of Dr. E. Knecht many years ago. Individual laboratories test dyes from their own points of view and doubtless collect much valuable information. The circulars from the dye manufacturers are more informative than they were in the past, but their purpose is to sell the makers' products, and therefore cannot be expected to detect and publicise all the snags.

Mr. K. E. WOODWARD: Slubbing dyed by the can (pressure) method is retarded in felting or milling properties as compared with open (Hussong) dyeing, which indicates that the scales of the wool fibre have become set to some extent, and it would be reasonable to expect a leaner yarn to be spun from pressure-dyed slubbing.

Mr. R. J. ROBERTS: In my experience metachrome-dyed wool is definitely harsher in handle than wool dyed with neutral dyeing acid dyes at the same pH.

Mr. A. ARMITAGE*: The lack of loftiness in most cylinder-dyed slubbing is obviously due to the crabbing action of the wash liquor which is forced through the tops under pressure after dyeing. This can be avoided by cooling the tops off slowly without the use of any forced circulation or pressure, and if the tops are then reeled and dried in a low-temperature hank-drying machine, it is possible to obtain a lofty-handling top without the attendant fibre damage and increased noil content from hank-dyed slubbing.

Mr. M. R. FOX*: In the Williams Continuous Fiber Processing Machine, developed by the General Dyestuff Corpn.[20], use is made of a very small-volume dyebath contained in a U-tube, and the loose material or slubbing to be dyed is carried through the dyeing chamber by means of a mesh conveyor belt. It is claimed that running speeds of 33 yd./min. are obtained and also that vat dyes have been satisfactorily applied to wool slubbing.

Dr. GAUNT*: The use of this machine would probably be limited to the vat and fast acid dyes on account of the length of time required to develop chrome dyes.

Mr. C. P. ATKINSON*: It has been suggested[21] that considerable improvements can be obtained in drying on cylinder-type machines by removing continuously the stagnant vapour layer by means of metal covers fitted round the cylinders, air being drawn into the ends of the covers and exhausted through slots running across the full width of the covers. Would this method be applicable to the drying of slivers on cylinders?

Dr. GAUNT*: This method does not appear to have been used for drying wool sliver.

* Communicated

FRIDAY AFTERNOON, 21st SEPTEMBER 1951

*Chairman*—Mr. R. J. HANNAY

# Fast Colour Printing

F. FARRINGTON, F. V. DAVIS, and P. W. SMITH

The development of fast colour printing is traced from the discoveries of indanthrone and the formaldehyde-sulphoxylates up to the present day. The relatively minor changes in machine printing technique since Bell's day are discussed, and screen printing is dealt with briefly.

Some of the printer's hopes for the future are then considered. These include provision of an effective discharge agent for anthraquinonoid vats, and a discharge agent which does not attack the disulphide bonds of wool. The possible improvement of pigment printing colours is discussed, and the deficiencies of agers are touched on. Finally, the problem of the ideal printing thickener is dealt with in some detail.

It is proposed to divide this paper into two parts—firstly a historical review (in outline only) of the developments, both chemical and mechanical, which have led to what is at present understood by the term "fast colour printing"; and secondly a discussion of the printer's hopes for future improvements and some of his wants which are as yet unfulfilled.

## Historical

### CHEMICAL

As a generalisation, fast colour printing as we know it was born at the beginning of this century. Before this, fast colours were virtually limited to Indigo prints by the Schlieper–Baum process (using glucose and strong caustic soda to reduce the Indigo), Turkey Red, and a limited range of insoluble azo dyes based on $\beta$-naphthol. Thomas and Holliday introduced Vacancein Red in 1880, by treating vegetable fibre first with $\beta$-naphthol dissolved in caustic soda and then with diazotised $\beta$-naphthylamine. This led to the development by Meister Lucius & Brüning of the four important members—Para Red, Metanitraniline Orange, $\alpha$-Naphthylamine Bordeaux, and Dianisidine Blue—where cloth, previously prepared with $\beta$-naphthol dissolved in alkali containing Turkey Red Oil, is printed with diazotised *p*-nitroaniline, *m*-nitroaniline, $\alpha$-naphthylamine, and dianisidine respectively. These colouring matters are not of high fastness by modern standards, while $\beta$-naphthol as a component has several disadvantages.

In 1901, Bohn discovered indanthrone, or Indanthren Blue R (IG), whose general fastness properties greatly exceeded those of Indigo. In the same year, Zündel in Moscow discovered the stabilising effect of formaldehyde on zinc hydrosulphite, and within two or three years the research work of Kurz[1] and of Schwartz, Baumann, and Thesmar[2] had led to industrial production of pure sodium formaldehyde-sulphoxylate, sold under a variety of names, but usually known to the printer as Rongalite (IG). It remains the universal reducing agent for vat printing, and the sulphur shortages of 1951 have brought home to the printer the unique place it occupies in his store.

Later in 1901, Bohn also produced flavanthrone (Indanthren Yellow G (IG)), and the halogenated indanthrones (Indanthren Blues GC, GCD, etc.) date from about the same time. This is no place to try to follow the chemist's ingenuity in building up new vat dye structures; from about 1905 they have followed one another in ever growing numbers, but one highlight was the discovery in 1920 of Caledon Jade Green by Scottish Dyes Ltd.

As the anthraquinonoid vat dyes were being developed, there was a parallel development of the indigoid vat dyes, resulting in a range of shades containing such useful members to the printer as Hydron Pink FF (Cassella, 1907), Ciba Scarlet G (S.C.I., 1907), and Ciba Brown G (1928).

One point which must not be overlooked is the progress made in the physical condition of the dye, from the coarse powders of the early days, which had to be prevatted with hydrosulphite and caustic soda, to the finely dispersed pastes of to-day, which give speck-free prints by merely mixing into the printing colour, and to the growing number of self-dispersing printing powders, which need only stirring into water or gum thickening, and are more convenient to store than paste brands. The use in the printing colour of hygroscopic agents such as glycerol or urea, coupled with better designs of ager, has improved colour fixation and uniformity very considerably.

During the war, the I.G. investigated the effect of introducing trifluoromethyl ($CF_3$) groups into vat dyes, and this resulted in the marketing of Indanthren Blue CLB (Basf) with greatly increased fastness to chlorine bleaches over the standard Indanthren Blues. Other trifluoromethyl-containing vat dyes were produced experimentally; FIAT Report 1313 mentions a greenish-yellow non-tendering dye with excellent light- and chlorine-fastness, which contains two such groups.

The normal method of printing vat dyes with British Gum thickening, alkali-metal carbonate, and Rongalite necessitates their being aged within a comparatively short time of printing. In 1927 the I.G. introduced the Colloresin process, where the vat dye is printed as a pigment in an alkali-insoluble methyl cellulose thickener. The printed goods may be stored for an almost indefinite time before further processing, which consists in padding through alkali and reducing agent and then ageing. More recently, a modified version, using locust-bean gum thickening (which is coagulated by alkali) has been employed. The disadvantage is that all-vat prints are necessary; the use of insoluble azo dyes alongside vats becomes impracticable.

In 1921, Bader[3] invented the first of the Indigosols by preparing the sodium salt of the disulphuric ester of leuco indigo. Following this, the range of Indigosol (DH) and Soledon (ICI) dyes became gradually available. Their advantage is that they

are soluble in water without special preparation, and can be printed on to cloth without difficulty. No ageing is required to fix the colour, but on subsequent treatment with an acid and oxidising agent, simultaneous hydrolysis of the ester and re-oxidation of the leuco compound to the parent vat occur. Particularly useful to the printer are methods where the printing colour carries an oxidising (or potentially oxidising) agent, a substance which yields acid on ageing (such as ammonium sulphate or thiocyanate), and an oxidation catalyst (such as ammonium vanadate or potassium ferrocyanide). Hydrolysis and re-oxidation to the parent vat then occur on merely steaming or ageing. The disadvantages of these dyes are their expense; some are all too easily overoxidised; and some are light-sensitive. They are of outstanding usefulness in discharge and resist styles, with vat or azoic grounds.

In 1912, Griesheim-Elektron A.-G. produced 2:3-hydroxynaphthoic anilide under the name Naphtol AS, and followed this with other arylides of this acid, laying the foundation for the fast insoluble azoic prints of to-day. The Naphtol AS series are in general much easier to apply uniformly to cloth than $\beta$-naphthol, and give shades after coupling which are brighter and of better all-round fastness. Some have only low substantivity, whereas others are highly substantive, and the printer tends to choose the less substantive members, to avoid trouble in afterwards removing Naphtol from the unprinted ground. The range of colours obtainable was widened by the introduction of arylides of other hydroxycarboxylic acids derived from naphthalene, anthracene, carbazole, benzocarbazole, etc. capable of giving a dull green, blacks, and browns on coupling, but yellows are unobtainable with the hydroxyarylanilides. The first yellow-producing Naphtol, AS–G (1921), was derived from tolidine and acetoacetic ester; it was followed ten years later by AS–LG and AS–L3G, but all have the disadvantage of being difficult to discharge. The introduction of Naphtol AS–L4G (2-acetoacetylamino-6-ethoxybenzothiazole) [4] in 1933 overcame this difficulty.

Among the diazotisable bases, mention must be made of Variamine Blue B (IG, 1929) [5], which gives fast, deep, bright blues immensely superior to the older dianisidine blues. Good browns are obtainable with Fast Brown V base (3-*o*-chloro-*p*-nitrobenzeneazo-4-amino-6-methoxytoluene) [6]. Finally, the idea of introducing trifluoromethyl groups has been applied to the diazotisable bases, resulting in compounds of excellent light-fastness; this group at present comprises Fast Scarlet Base VD [7], Fast Golden Orange Base GR [8], and Fast Golden Orange Base GGD.

It is naturally advantageous for the printer to be able to have stable, ready-for-use diazonium salts instead of having to prepare his own diazo liquors. The dyemakers have been able to satisfy this demand in the case of most of the bases, the main stabilisers for the diazo compounds being zinc chloride (to form the double salt with the diazo compound), sodium naphthalenesulphonates, and fluoroboric acid.

Although the fastness of individual members of the legion of azoic combinations varies enormously, selected combinations are equal to vat dyes in all-round fastness.

From the early days, the printer has sought for ways of simplifying the use of azoic dyes, by having the Naphtol and diazo component in the same printing paste; in practice this means having a compound present which will not couple with the Naphtol until some simple operation such as steaming or acidification liberates the diazo compound, which is then free to couple. The first successful attempt was represented by the Rapid Fast dyes (Griesheim Elektron 1915) [9], which are mixtures of stable *anti*-diazotates with alkali-metal salts of Naphtol AS or other Naphtols. They can be printed from an alkaline paste on to unprepared cloth, and on subsequently ageing in acid steam, or neutral ageing and then souring, the *anti*-diazotate is converted to the *syn*-diazotate, which couples with the Naphtol.

The Rapidogen series (IG, 1930) [9] uses another principle, where the diazo compound is converted to a stable diazoamino compound by reaction with a suitable amine, commonly sarcosine or methyltaurine, and this stable compound is then mixed with one of the Naphtol series. The Rapidogens, like the Rapid Fast series, are printed direct on unprepared cloth from an alkaline medium. On treatment with acid steam, the diazoamino compound is split, and coupling occurs.

The necessity for treating prints with steam containing acetic and formic acid has been a practical drawback, and a later improvement was the use of an organic base to dissolve the Rapidogen, which was of sufficiently high pH in solution, but volatile in steam, so that hydrolysis and coupling occurs in a normal "neutral" ager. Diethylaminoethanol has the requisite properties, and was introduced as Rapidogen Developer N (IG) [10]. Various modifications have been suggested, including additions of acid-yielding esters or solvents for the Rapidogen dye.

A third method is that of the Rapidazols (IG) [11]. Diazonium salts form stable diazosulphonates with sodium sulphite, and certain of these give the active diazo compound on heating. The range is limited to blues, blacks, and oranges.

A different method of attack is to form the insoluble coupled azo dye, and then to render it soluble by chemical modification. Ciba produced the Neocotones [12] by introducing into the azo dye the substituent $CO{\cdot}R{\cdot}SO_3H$, where R is an aromatic ring. After printing, the solubilising substituent is split off by treating with an alkali, commonly a mixture of sodium and barium hydroxides.

A recent alternative procedure (Francolor, 1949) [13–15] is to convert the base to a sulphamic acid, which is diazotised without isolation. On coupling with a Naphtol, a colourless material is obtained, which is readily soluble in hot water, and is reasonably stable in solution. It can be printed from a slightly alkaline medium, and

hydrolysis occurs on subsequent acid treatment, leaving the insoluble azo dye.

The general principle of converting an insoluble pigment to a soluble derivative, which may be used by the printer and reconverted to the insoluble pigment on and in the fibre by a simple after-treatment, has been followed in other directions. Alcian Blue (ICI) is the pigment Monastral Blue converted to a soluble quaternary ammonium compound, which is stable in acid media but is hydrolysed by alkali with re-formation of Monastral Blue. The printer uses it in buffered acid media containing a salt yielding alkali on steaming, so that a simple ageing or steaming causes the necessary change in pH, and the insoluble dye is formed. In Germany, Monastral Blue has been converted to a derivative having a soluble leuco compound, and applied by the ordinary printing methods for vat dyes.

A rather different method has been Francolor's application in Solanile Black [14,16], and Durand & Huguenin's in Indosol Black, of sulphamic acid formation to such amines as aminodiphenylamine for oxidation dyes. The sulphamic acid may be printed in a neutral medium with an acid-yielding salt (ammonium thiocyanate or oxalate), sodium chlorate, and a vanadate as an oxidation catalyst. On steaming, acidity develops, hydrolysis of the sulphamic acid occurs, and oxidation to the insoluble black pigment proceeds. The conditions of acidity and oxidation are less severe than is necessary for printing normal diphenyl blacks.

The Farbenfabriken Bayer (FBy) have succeeded in synthesising Monastral Blue on the fibre, by applying Phthalogen Blue and then heat-treating.

Finally, brief mention must be made of the principle of applying an insoluble pigment of high light- and wash-fastness, not by conventional dyeing or printing methods, but together with a resinous binder in the form of an emulsion containing as the non-aqueous phase a resin dissolved in a volatile organic solvent. On drying and curing, solvent removal and resin polymerisation serve to fix the pigment (Aridyes, Oremas, etc.). These will be referred to again, later.

Chemically, then, the picture emerging from this rapid survey is a clear one. Fast colour printing means the formation within and on the fibre of water-insoluble pigments of inherently high light-fastness. In the main, the chemist's energies have been devoted to the synthesis of suitable pigments, and of devising means for their easy application, either as soluble derivatives which may afterwards be converted back to the insoluble pigment by some simple treatment, or by binding them mechanically to the fibre by synthetic resins. Unfortunately, as each new type of product overcomes the difficulties associated with its forerunners, it seems to bring fresh troubles of its own.

### MECHANICAL

The roller printing machine as it exists to-day is derived from the invention of Bell, who first brought such a machine into production in 1785 and is generally conceded to be the actual inventor. According to the point of view which one may adopt, the relatively small changes which have taken place in the 165 years between Bell's invention and to-day are either a great tribute to his inventiveness or an indictment of textile printing practice and engineering technique. It is true that improvements have been made, but they are incidental rather than fundamental.

Modern wash-blankets incorporating back-grey and fabricated from the increasing range of polymers and synthetic fibres now available are a good example of the utilisation of modern methods to carry out virtually the identical task entrusted to back-grey and blanket on the early machines.

Photogravure engraving has been developed, and modern chromium-plated rollers have a life far greater than the old copper types in addition to assisting the printer practically to eliminate scratching, but here, again, Bell would recognise little basic difference between his albeit crude roller and its modern counterpart.

In furnishing the colour to the engraved roller, the old-type roller-and-brush furnishers are outmoded by brushes of nylon bristle, which are of a high degree of efficiency and of much longer life.

The present-day printing machine is thus a very direct descendant of its Scotch forebear, and is still liable—if not expertly handled—to show those defects which have existed from the first. Careless printing to-day may still result in the "dirtying" of colours by rollers working before them in the machine, and the "crushing" of the first printed colours of a multicoloured design still detracts from the boldness of colouring and general attractiveness of a machine print, as even a cursory comparison of a machine print with a screen print will show.

Screen printing is, as yet, too young to have shown any major change in its practice. The hand methods of screen printing are a very obvious target for replacement by mechanical methods, and numerous machines are now available, but informed opinion is still divided as to their merits [17]. Again, the replacement of the silk gauze by nylon or other synthetic fibres or monofils, or by metallic wire gauze, has received some attention, but the bulk of the screens used continue to be made of silk.

## The Future

As regards colouring matters themselves, the weak points of the present range are perfectly well known to both users and makers. The anthraquinonoid vats have no really good bright red—all fall short of what is required in some way or another; despite the number of yellow members, there are few indeed that are good from the printer's point of view and do not accelerate tendering in light; fewer still when they are mixed with other colours to give bright yellow–greens, etc. The azoic range is lacking in good dischargeable greens. These are only a few representative cases.

A gap specific to the printer is an effective discharge agent for anthraquinonoid vats. Since the Badische Anilin- und Soda-Fabrik introduced Leucotrope in 1909, there has been no significant

advance in this field. Albigen A (polyvinyl-pyrrolidone) [18], which combines with leuco vats to give insoluble complexes, is a new and very effective aid to the stripping of vat dyes, but it seems to have no value as a discharge agent for prints, and as the benzylation reaction of Leucotrope is limited to certain vat dyes, many of the fastest members used by the printer remain undischargeable.

The fast colour printing of wool lags far behind that of cellulosic materials. Despite advances made in the chemistry of the wool fibre, it remains impossible to print wool in fast shades without causing significant tendering, while effective discharge or resist styles remain unattainable. It may be that the chemical mechanism of wool dyeing will always render a perfect resist print impossible — tone-in-tone is the best that can be achieved at present— but is a discharge agent which does not attack disulphide bonds completely out of the question? The use of protective agents on the wool is an alternative possibility.

The printer hopes for big developments in the use of pigment colours. We now have ranges of pigment printing compositions which require only a cooking treatment— or maybe even drying over tins— to give prints of reasonable fastness to light and to washing, but, as is well known, the fastness to dry or wet rubbing is poor. There are other troubles, too, such as a tendency for the organic solvent to spread outside the printed area by capillarity, bearing with it some resin, and in some cases pigment either in an almost colloidal state or in actual solution. Clearly there is room for considerable work on the preparation of actual pigments having not only the maximum light-fastness and alkali-resistance, but also the most suitable physical condition and insolubility in organic solvents. It is not doubted that much has already been done on these lines. Apart from the actual pigment, the ideal binder has obviously not yet been found. Will improved types of binder give us better rubbing fastness, or will it always be that surface deposition of a pigment together with the maximum amount of resin compatible with an acceptably soft handle on the cloth can only result in looseness to rubbing?

The pigment printing colours have a special appeal in the printing of the newer synthetic fibres— Terylene, Orlon, Dynel, etc.— where the water imbibition is extremely low, and normal dye-transfer from a thickening film into the fibres themselves limits both the depth of shade and the fastness of conventional dyes. There is one other point of general interest: in the present pigment prints on smooth lustrous cloths, the colour interferes with the lustre and appears to be on the surface. The effect is quite different from, say, a vat print of the same shade. If the printer of the future attempts to use pigment printing on all types of fabric, and this characteristic persists, there is a risk that the ultimate customer may be prejudiced by this "different" appearance. How far is it unavoidable, and how far can it be altered by changing the physical properties of pigments, the ratio of pigment to fixing resins, and the nature of the resins?

Further extensions of the principle of converting insoluble colouring matters into easily applied derivatives, which after printing can be reconverted to insoluble pigment within the fibre— as distinct from resin-coated pigment adhering to the outside of the fibre— by some simple process, are clearly to be expected. The present methods all have their disadvantages, and it is to entirely new methods rather than to extension of existing ones that the printer looks. His ideal remains to print his colour and then merely to submit his print to a readily controlled simple process, such as heating in a constant-temperature chamber, or passing through a chemical bath which cannot harm his cloth or give variable results from the same printing paste.

This naturally turns one's thoughts to agers and steamers, the weaknesses of which are only too well known to printers. They would like to replace their agers by an apparatus not depending on the vagaries of steam temperature and moistness, and the air content of the steam, for their efficiency. In this connection the studies on dye-transfer in the steamer by H. A. Turner [19,20] are welcomed; as this work progresses, it may give a clearer picture of what exactly goes on when the cloth has entered the ager. The Standfast molten-metal machine has recently engaged the attention of dyers, and though it is unlikely that the principle can be adapted to vat dyes printed together with alkali-metal carbonate and Rongalite in the thickening, can it be successfully used to replace an ager in a Colloresin type of process?

Printing thickeners themselves deserve more than a few words of consideration. Whilst the properties required for a satisfactory thickening have been generally realised by practical printers in an empirical way, it is only recently that the physical properties of thickenings have been systematically investigated, and there is already a clearer picture of what is wanted. At present, the perfect universal thickening does not exist, and the printer has to compromise. Natural products suffer from the defects of variable quality and the presence of grit and other impurities which are difficult to remove; frequently, long boiling is required for their proper solution, and this in itself may give variable products. There have been quite a number of attempts to produce what, for want of a better term, may be called "synthetic thickenings", of standardised quality and ready solubility in the cold, free from insoluble vegetable matter and grit. Notable in this field have been the researches of W. A. Scholten's Chemische Fabrieken N.V.[21] on chemically modified starches, and the present indication certainly is that starch is a more promising raw material for thickenings than cellulose. The ideal thickening demands, in addition to uniformity, purity, and ready solubility, a whole range of properties. First, the rheological properties of the thickening must be right: its apparent viscosity must be high enough at the high rates of shear occurring in printing machines to give sharp outlines, while its apparent viscosity at

low rates of shear must be low enough to allow proper furnishing. The printer's task is easier if the proportion of thickening solids to dye is as low as possible, yet there are indications that thickeners of low solids content have a high degree of viscous anomaly, and do not readily fulfil the conditions for machine printing. Will this necessarily always be so? Then, again, the ideal thickener must have good keeping qualities and should not be affected in any major way by acids, alkalis, reducing agents, oxidising agents, dispersing agents, hygroscopic agents, solvents, or the dyes themselves; i.e. it must not gel or show marked liquefaction, nor become "ropy" or "short". Conversely, it must not cause aggregation of dye dispersions or show unwanted reducing properties. It must be easily removed by washing-off after printing and ageing. To this formidable list, the printer adds two further requirements—it must at all times be in ample supply, and it must be cheap!

There is, of course, an alternative to the usual mucilage type of thickener, namely the emulsion thickener, which has already been used in some of the pigment printing colours. The principle of having a high-viscosity thickening containing approximately half water and half volatile organic liquid, with only 1–2% of solid matter in the shape of emulsifying agent, is attractive for several reasons. There is virtually no solid to hinder dye-transfer from thickening to fibre; there is no need for vigorous after-washing to give soft handle in the printed areas. At present, the difficulties of making emulsions stable to the high electrolyte concentrations used in vat and other fast colour printing pastes, and of securing satisfactory rheological behaviour, make the prospect of extending the use of these emulsions remote, but this may not always be so.

No claim is made that this review is complete; indeed it is hoped that it will serve as a stimulus, and that other wants and hopes for the future will be brought to notice during the discussion.

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## Discussion

Mr. A. S. Fern: Do the authors think that any far-reaching improvements can be envisaged in the stage of forming the aggregates of insoluble colouring matter, which they have shown to be essential for producing fast prints? For example, will the techniques available for soaping azoic combinations, vat dyes and developed Indigosols, for oxidising vat dyes, or for developing Indigosols give aggregates of the optimum size and position in the fibre?

Mr. Davis: It is, of course, well known that the state of aggregation of dyes within the fibre is affected by treatments such as steaming and soaping, and the printer already makes use of this where experience shows it to be advantageous. At the moment it is rather difficult to foresee any new development on these lines which will show any further advantage.

Mr. C. P. Atkinson: Attempts are being made to increase the speed of the roller printing machine without impairing the quality of the print. The American John Waldron Heliofast high-speed machine dispenses with the central impression cylinder and substitutes a series of independent nips with small backing rollers behind the printing roller. It is claimed that the much sharper nip gives a clean impression at a high speed. The makers state that accurate register at speeds of 230 yd./min. can be maintained, and that the small arc of nip contact permits a lighter pressure with less stretching between the nips. If this is correct, then the production of shirtings and linings can be increased.

With reference to chromium-plated rollers, if a scratch does occur, then it is not easy to remove it.

In America pigment colours are more often used than in this country, and research work at present being carried out there may eventually indicate methods of overcoming their poor rubbing fastness.

Mr. Davis: No pigment colour yet reaches the standard required for all styles. There is no doubt that in America there is not the same insistence on high quality that there is here, and what, for example, may be accepted for a bulk-produced shirting there would not be satisfactory for a high-class poplin here. There is probably a legitimate use in this country for pigment colours on some furnishings and special styles where rubbing fastness is unimportant.

Mr. K. Lowit: Only vat dyes give a range for the artist to use as his palette. The paper does not mention surface roller printing.

Mr. J. A. Kiernan: The type of dispersing agent used has a great bearing on the thickening medium, and it is frequently found that dyes from different makers react differently in the presence of a given thickening. There appears to be room for more uniformity in this direction.

Mr. F. Crompton: Is Brown V Salt homogeneous or a mixture?

Mr. Davis: Brown V Salt is the stabilised diazo compound from the homogeneous Brown V Base. It is said to be stabilised as the zinc chloride double salt, with small amounts of oxalic acid, albumen, and dextrin added.

Mr. Crompton: If a printing machine with more than one printing cylinder is used, will there be a shrinkage of the cloth from nip to nip?

Mr. Davis: The Waldron Co. claims better registration with its printing machine than with the orthodox type, as the cloth tension between the printing nips can be much lower than on the single-cylinder machine.

Mr. R. Thornton: Starch and gum manufacturers as well as dyemakers continue to simplify their products in order to make the printer's task easier. It now appears most timely to examine critically emulsion thickenings with the following five factors in mind—

(*a*) Conventional thickenings involve, directly or indirectly, the world's food supplies, and experts affirm that food supplies are inadequate.

(*b*) Conventional thickenings are by no means ideally suited for printing many of the newer hydrophobic man-made fibres. However experimental such fibre projects may be to-day, an extension to normal commercial usage is to be anticipated.

(*c*) Recent developments in dyes and their application tend to make increasing use of organic solvents, and it is probably true to say that the organic solvent is a necessary component in the reaction involved in the dye transfer. This being the case, a conventional thickening involving a high proportion of an aqueous phase does not necessarily form an ideal medium.

(*d*) Conventional thickenings require removal at some stage of processing after the mechanical operation of printing. An emulsion thickening can, if necessary, be completely removed at the drying-after-printing stage.

(*e*) In the pigment-printing field, for certain classes of work, emulsion thickenings have successfully established themselves and thereby have broken down much prejudice in the industry.

Mr. R. J. Hannay: It should be stressed that a large amount of work has been done both in this country and in other countries, particularly the U.S.A., in the formulation of emulsions for use as printing thickeners or combined thickeners and fixatives; a certain amount of work has also been done on wholly organic media.

The use of emulsions has presented some very difficult problems associated with their instability. Generally speaking, emulsion thickenings break down under the mechanical action of the furnishing rollers and the churning effect in the colour box; also, even though they may be sufficiently stable to print immediately the emulsion touches the fabric, they are again broken by the preferential absorption of the aqueous phase, which results in a surface print of poor penetration and low rubbing fastness. On the other hand, it is true to say that very sharp definition is given to fine detail in this process.

Work is continuing along these lines, but progress is slow owing to the many factors which influence this technique. Consideration has to be given to the particular type of emulsion— water-in-oil or oil-in-water or a combination of the two— needed to attain the best results. The effect of additions of various chemicals used in printing has also to be taken into account, and not infrequently such additions have a detrimental effect on the stability of the finished emulsion.

My own view is that the emulsion technique is not the best line of approach, and practical experience has shown that for special effects the medium made by the use of purely organic solvent and thickener can yield much better results. In such a case penetration is good, furnishing properties are good, and the dye is exceedingly well dissolved or dispersed in the medium. Here again, however, there are difficulties, for one must take into account the various risks which arise when using organic solvents— fire hazards are usually greater, toxic risks and health hazards which may arise from certain solvents must be studied, and (perhaps of a more practical nature) the difficulties of cleaning rollers and blankets when using such media have to be considered.

Mr. D. A. Derrett-Smith: It sometimes happens in a multicoloured print on a cambric, for example, that one colour is behind the others in penetration. What are the important conditions which must be observed in order to secure a well penetrated print?

Mr. Davis: This is too wide a subject to be dealt with adequately during this discussion. Efficiency of scouring and bleaching, and proper conditioning of cloth before printing, both have a great influence on penetration, though in the specific case of one colour not penetrating as well as others in a multicolour print the reason must lie elsewhere. There may be mechanical differences, such as depth of engraving or pressure on the printing rollers. Then again, there may be differences in the thickening; the offending colour may be thickened with starch, whereas the others are thickened with British Gum. Even if all the colours are made up with the same thickener, there may be a difference in behaviour on the machine, as the apparent viscosity as judged by the colour-shop man or printer, by stirring, is not necessarily a guide to its apparent viscosity under shear in the machine. Furnishing of the engraving occurs at a medium rate of shear, but the doctor blade imposes a very high shear-rate, to quote only two items which may affect the actual amount of printing paste applied to unit area of cloth. If one colour is "borderline" as judged by stirring, it may easily be too viscous to furnish properly, or not viscous enough at very high shear, so that the doctor "strips" the colour out of the engraving. In short there are too many factors to give a concise answer, especially when the type of colours used, etc. is not known. The one thing certain is that apparent viscosity (as judged by the printer) is not the sole governing factor.

Mr. C. J. WRIGHT*: The statement that the phthalocyanine derivative Durazol Blue 8GS gives a much better colour yield with aqueous emulsions than with mucilage thickeners should not be taken as serious evidence in favour of aqueous emulsions, since it is an extreme case. It is probable that the better result in colour value is due largely to the extreme sensitiveness of this dye towards the presence of even small quantities of electrolytes, such as could be present in aqueous emulsions for printing. It would therefore be misleading to accept this evidence, unless substantiated by similar results with a variety of dyes.

Mr. DAVIS*: I fail to see Mr. Wright's point. Durazol Blue 8GS is an S.D.C. Class B direct dye, but surely it is no more electrolyte-sensitive than many other dyes. In any case, the presence or absence of small amounts of electrolyte in a thickener is of very small moment when one considers the large amounts of electrolytes that the printer always adds, while a tragacanth thickener itself (particularly if neutralised) probably contains at least as much electrolyte as any emulsion thickener.

Mr. WRIGHT*: In general, it is agreed that small amounts of electrolyte in a thickener are of little importance, but it is important to note that Durazol Blue 8GS is much more electrolyte-sensitive in aqueous medium than many other dyes.

* Communicated

# Studies in the Fundamental Processes of Textile Printing
## III—The Transfer of Indigosols to Cellulose during Steaming

A. M. A. El Borai and H. A. Turner

The transfer during steaming of a selected range of the sodium sulphuric esters of leuco vat dyes from a film of starch to an attached film of regenerated cellulose has been studied. Curves relating time of steaming with dye transferred suggest that this transfer is a complicated process. Additions of assistants, such as alkali-metal carbonates or sodium *N*-benzylsulphanilate, may cause marked changes in the course of the dye transfer. An explanation is put forward which relates the behaviour of the Indigosols in part with the behaviour of some acid dyes which are suitable for printing on regenerated cellulose and in part with the decomposition of the Indigosol as steaming proceeds.

### Introduction

Munshi and Turner[1] have described an experimental method designed to allow the study of the migration of a water-soluble dye from an impressed print to the adjacent fibre substance. This method was first used to investigate the migration during steaming of purified direct cotton dyes, from a variety of thickeners, to regenerated cellulose. A study was then made of the corresponding process for some of the acid dyes which are used for printing viscose and cuprammonium rayons[2]. Certain of these dyes showed unusual migration properties, of which the principal details will be summarised below. It was then decided to extend the investigation to the Indigosols, which, in respect of their property of being adsorbed on cellulose from aqueous solutions, may be said to stand, in general, between the direct cotton dyes and the acid dyes suitable for printing. Seven Indigosols* were examined deriving from both anthraquinonoid and indigoid parent vat dyes, and it was found that, while their migration properties were closer to those of the acid dyes than to those of the direct dyes, most of them on prolonged steaming gave evidence of an increased complexity in the course of the dye transfer. These results were not altogether unexpected, since, in the first instance, dyes were examined which were as free as possible from inorganic electrolytes. This meant that the sodium carbonate usually present in commercial brands of these dyes was absent, or present in a much reduced proportion, and that there was no deliberate inhibition of decomposition of the leuco esters. In addition, many of the Indigosols are sparingly soluble in water, especially in the cold, and at the concentrations used were unlikely to be in complete solution in the restricted amount of water supplied to the system by the steam. Before discussing the transfer behaviour of these dyes in detail, it will help if a short statement is given of the corresponding migration properties of the acid printing dyes.

#### Migration of Acid Printing Dyes

The exploratory work in this field was largely carried out by R. B. Patel[2], and it is on the results of this work that the present summary will be based. Investigation of the acid dyes is at present being extended by R. E. Pomfret[3], and his results are tending to demonstrate, to an increasing extent as the work progresses, the fact that individual dyes can show very marked deviations from the general behaviour as a class. Nevertheless, this general behaviour may be summarised as follows—

(*a*) Acid dyes suitable for direct printing on cellulose belong almost exclusively to the soluble, levelling group. They were classified by Meitner[4] on the basis of their particle size in dilute solutions in water. Those of the lowest particle size give very poor exhaustion on the fibre. This is assumed to be due to the fact that they are molecularly dispersed and cannot be retained in the pores of the fibre, and further that they lack the property of re-aggregation once within the fibre. Those at the upper end of the range of particle size are assumed to be too large to enter the fibre. The most useful printing members therefore occupy an intermediate position in the scale; it is assumed that they consist of particles small enough to enter the fibre, but capable of being fixed therein by subsequent aggregation.

(*b*) Coomassie Brilliant Blue FF (ICI) is a dye which shows to a pronounced degree those migration effects which are also found in other acid printing dyes when the starch–cellulose system is steamed. It may therefore serve as a general example. Transfer of this dye between the two phases, starch and cellulose, can take place with great ease in either direction. Steaming is not essential, since, if a layer of starch paste containing dye is applied to the surface of a Cellophane sheet and is dried at room temperature, increasing concentration in the starch as the water is removed leads to a corresponding exhaustion of dye on to the cellulose. Similarly, in steaming experiments, the exhaustion of dye from the starch to the cellulose layer increases with increase of initial dye concentration in the starch, an effect which is the reverse of that obtained when a substantive dye is dyed on cellulose. The curve showing change of exhaustion with time of steaming is given in Fig. 1. It will be seen that the exhaustion reaches a maximum in about 1 hr., after which some dye returns to the starch. This, again, is behaviour which has not been observed with dyes having a pronounced substantivity for cellulose. When a swelling agent such as urea is also present, the general level of exhaustion is diminished, and the maximum occurs earlier. A dye such as Naphthalene Scarlet R (ICI), which is much lower down on Meitner's list, also shows a maximum in the exhaustion–time of

* For the sake of simplicity, the term *Indigosol* will be used in this work to describe sodium sulphuric esters of leuco vat dyes from whatever source. When individual dyes are referred to, they will, of course, be given the name used by the manufacturer.

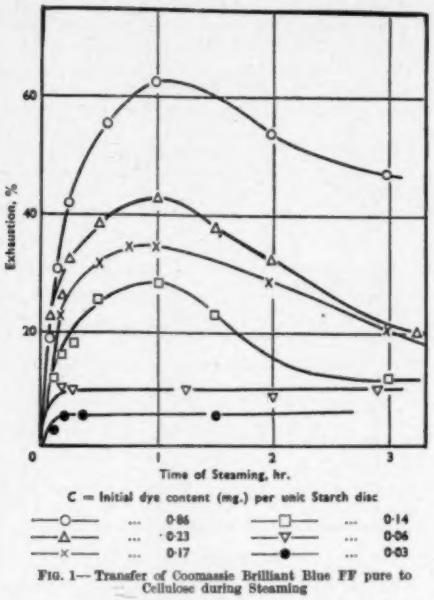



FIG. 1— Transfer of Coomassie Brilliant Blue FF pure to Cellulose during Steaming

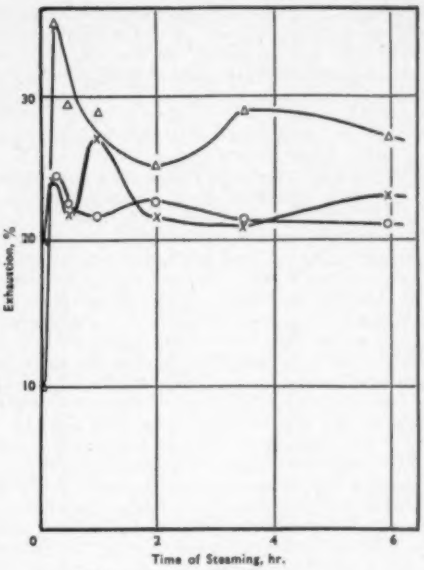



FIG. 3— Transfer of Indigosol Blue O4B to Cellulose during Steaming

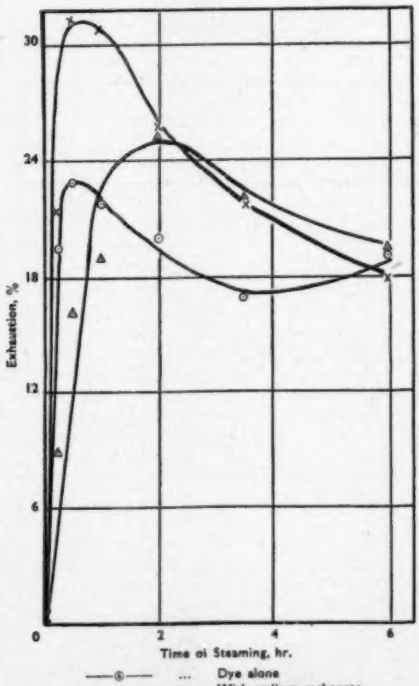



FIG. 2— Transfer of Indigosol Green IB to Cellulose during Steaming

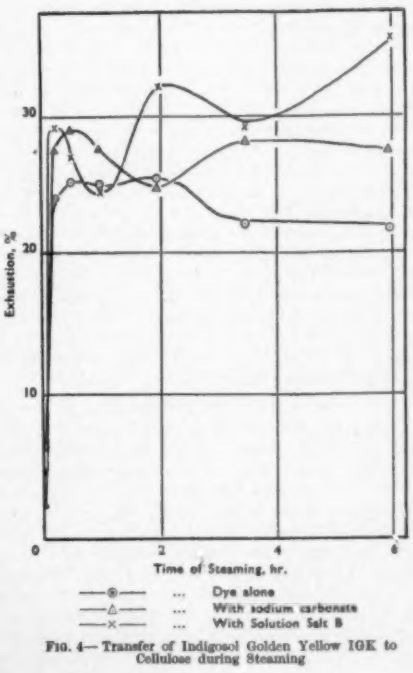



FIG. 4— Transfer of Indigosol Golden Yellow IGK to Cellulose during Steaming

steaming curve, although here the general level of exhaustion is lower and the maximum occurs earlier. A dye higher up on the list, such as Coomassie Blue R (ICI), gives an exhaustion curve in which there is no maximum, but a continuous rise which diminishes asymptotically to an equilibrium exhaustion. Only when urea is present is a maximum found with this dye.

(*c*) As a qualitative explanation of these facts, it has been assumed, in conformity with the observed dyeing properties of acid dyes on cellulose, that very little true affinity exists, i.e. that chemical bonding between dye and fibre molecules is infrequent and weak. At the beginning of steaming, dye at high concentration in the water contained in the starch layer will diffuse under a concentration gradient into the water contained in the cellulose until the concentrations in the water in each phase are equal. Ideally, at this stage, the proportion of total dye in each phase will be the same as the proportion of total solvent water. Thus, any change in the distribution of water between the two phases will be accompanied by a change in the exhaustion of the dye. There is qualitative, and some incompletely quantitative, evidence that the starch continues to swell and take up water as steaming proceeds, while the water content of the cellulose remains constant or diminishes slightly. Thus, in the later stages of steaming, there will be a tendency for some of the dye which has first diffused into the cellulose to return to the starch, where increasing water uptake is causing dilution of the dye solution present. This explanation has been found to apply to other observed behaviour of the acid dyes. For instance, in a starch–cellulose system with the same area of interphase surface and the same weight of dye present, the distribution of dye, when at a steady value, has been found to be proportional to the relative volumes of the two phases, when they are varied by changing the relative thickness of the respective films. Further examination of the results with certain acid dyes by Patel [2], Mhatre, and Pomfret [3] has shown that, while the bulk of the dye within the system may be regarded as mobile and carried from phase to phase in solution during the steaming, a small proportion appears to be more firmly fixed to the starch. This seems to account for the fact that the exhaustion at a fixed time of steaming increases with increasing dye content of the system, and does not remain constant as the simplest application of the above hypothesis would imply.

### MIGRATION OF INDIGOSOLS

The transfer behaviour on steaming of Indigosol Green IB (DH) (Table I) with the accompanying electrolyte content reduced to a minimum is shown in Fig. 2. It will be seen that the curve relating exhaustion with time bears a qualitative resemblance at least to that of Coomassie Brilliant Blue FF, in that it also passes through a maximum during the course of prolonged steaming. Were this the only evidence available, it might be thought that the mechanism which has been suggested for the transfer of, say, Coomassie Brilliant Blue FF would be appropriate for the Indigosols also, in

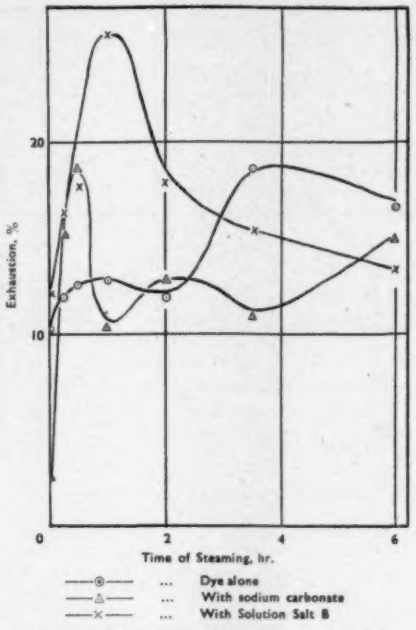



FIG. 5— Transfer of Cibantine Brilliant Pink R to Cellulose during Steaming

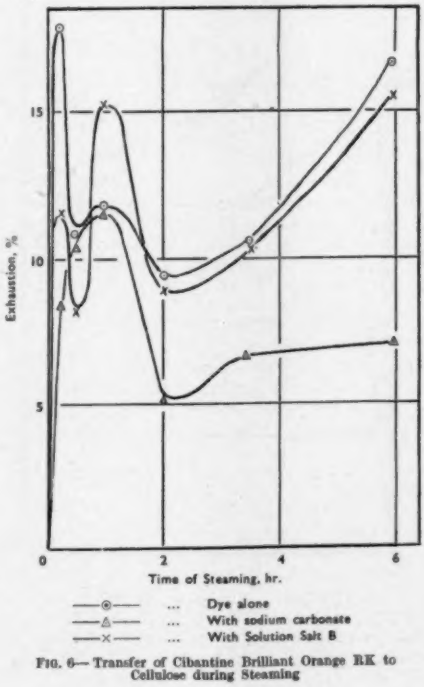



FIG. 6— Transfer of Cibantine Brilliant Orange RK to Cellulose during Steaming

spite of the fact that Indigosol Green IB has a much more pronounced affinity for cellulose when dyed from solution. The other Indigosols examined (Table I), for which exhaustion–time of steaming curves are given in Fig. 3–8 respectively, taken together, exhibit much more complicated transfer properties. It will be seen that all except Cibantine Brown G have two maxima in the curve. Where there are two maxima, they rise to different relative heights and occur at different times of steaming for each of the different dyes.

TABLE I

| Fig. | Indigosol | Parent Vat Dye |
|---|---|---|
| 2 | Indigosol Green IB (DH) | 16:17-Dimethoxydibenzanthrone |
| 3 | Indigosol Blue O4B (DH) | 5:7:5′:7′-Tetrabromoindigo |
| 4 | Indigosol Golden Yellow IGK (DH) | 4:5:9:10-Dibenzopyrene-3:8-quinone |
| 5 | Cibantine Brilliant Pink R (Ciba) | 6:6′-Dichloro-4:4′-dimethylthioindigo |
| 6 | Cibantine Brilliant Orange RK (Ciba) | 4:10-Dibromoanthanthrone |
| 7 | Cibantine Brown G (Ciba) | 4:5:4′:5′-Dibenzothioindigo |
| 8 | Soledon Blue 2RCS (ICI) | 3:3′-Dichloroindanthrone |

Alongside the curve for the dye without added assistant in each of Fig. 3–8 are also shown a similar curve representing the exhaustion when a standard addition of sodium carbonate has been made during preparation of the paste, and another with a similar standard addition of Solution Salt B (sodium *N*-benzylsulphanilate). The function and supposed action of each of these additions will be discussed more fully later. At present, all that is necessary is to call attention to the fact that each of these additions modifies the exhaustion–time curve for each of the dyes examined, and that this modification, which consists in a change of the relative height of the peaks and in an alteration of the steaming times at which they occur, is different in detail for every dye.

One other interesting property, found only in certain of the Indigosols, viz. Indigosol Blue O4B, Cibantine Brilliant Pink R, and Soledon Blue 2RCS, is the marked tendency towards rapid partial transfer in the cold when starch and cellulose films are brought together prior to steaming. Thus, approx. 20% of the Indigosol Blue O4B initially present in the starch film is transferred to the cellulose in the two or three minutes that is necessary to squeegee the dry, dye-containing starch film into contact with water-soaked Cellophane.

### MECHANISM OF INDIGOSOL TRANSFER

A hypothetical mechanism is proposed to explain results of the kind just described. Its detailed application to the results obtained with different dyes and in the presence of different assistants will be discussed at length in a later section. Briefly, it runs as follows. From the evidence obtained with the two dyes Indigosol Green IB and Cibantine Brown G, it is assumed that the Indigosols, if they were completely stable chemically during the whole

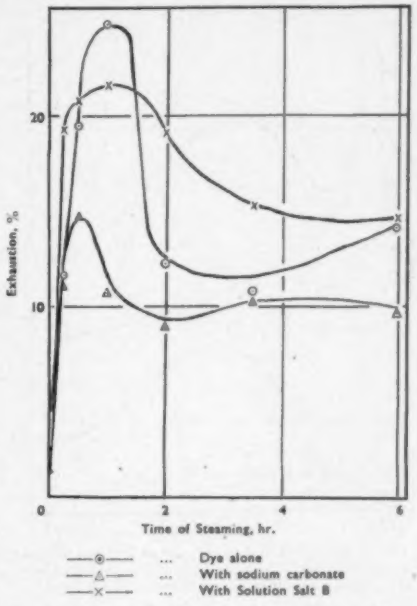



FIG. 7—Transfer of Cibantine Brown G to Cellulose during Steaming

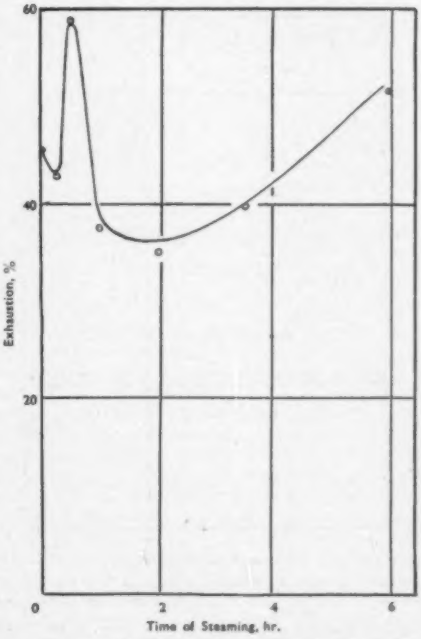
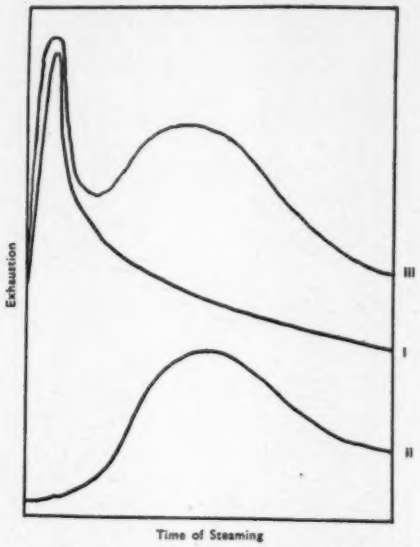
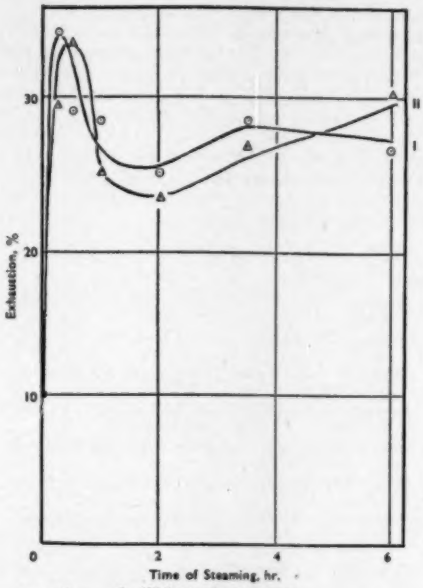



FIG. 8—Transfer of Commercial Soledon Blue 2RCS (with Further Addition of Sodium Carbonate) to Cellulose during Steaming



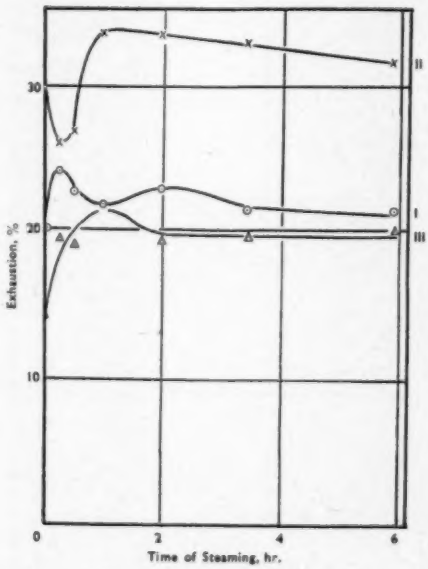

I ... Proportion of total dye in cellulose in unchanged form
II ... Proportion of total dye in cellulose in modified form
III ... Proportion of total dye in cellulose in both forms

FIG. 9— Hypothetical Curves for Transfer of an Indigosol to Cellulose with Coincident Decomposition




—⊙— I—Without prior treatment
—△— II—Film steamed for 1 hr. before transfer

FIG. 11— Effect of Prior Heat Treatment on Transfer of Indigosol Blue O4B from Starch Films containing also Sodium Carbonate




—⊙— I—Normal, without prior treatment
—×— II—Starch film with Indigosol steamed apart 1 hr. before transfer
—△— III—Indigosol heated in solution at 100°C. for 1 hr. before making starch film for transfer

FIG. 10— Effect of Prior Heat Treatments on Transfer of Indigosol O4B to Cellulose during Steaming

period of steaming, would behave like an acid dye such as Coomassie Brilliant Blue FF, exhibiting a more or less rapid exhaustion on to the cellulose in the early stages of steaming, passing through a period of maximum exhaustion, and then migrating in the reverse direction, i.e. from cellulose to starch. However, with those dyes that show a double maximum in the exhaustion–time curve, it is assumed that steaming brings about some decomposition of the dye and that some of the combined sulphuric acid is removed. This will introduce a new dye species into the system, one with a different solubility and with different migration properties from the parent Indigosol. Whichever phase it is in, it will have more difficulty in migrating to the other, and therefore, presumably, it will, if considered alone, possess an exhaustion–time curve which, if it is still of the Coomassie Brilliant Blue FF form, will have a maximum that occurs at different values of the exhaustion and time of steaming. The curve obtained in these experiments will be a combination of the separate curves for the undecomposed and the decomposed Indigosols, account also being taken of the change of one dye into the other during the whole course of steaming. Fig. 9 has been drawn as an illustration of the supposed mechanism.

This hypothesis allows the effects of the different assistants to be discussed. When sodium carbonate is present, it stabilises the Indigosol to decomposition, and thus the production of the second form of the dye will be inhibited or delayed.

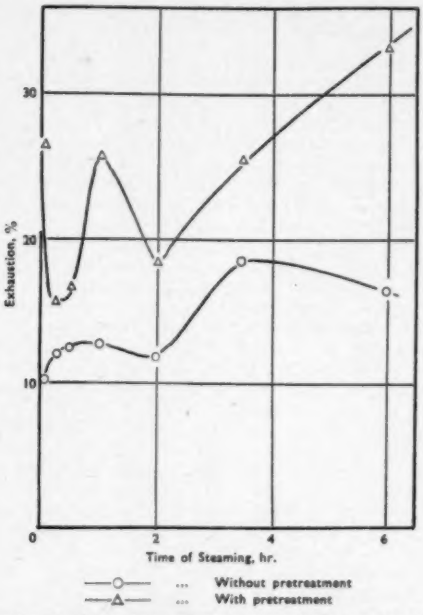



FIG. 12—Effect of Pretreatment of Starch Films containing Cibantine Brilliant Pink R in Steam for 1 hr. on Transfer to Cellulose during Later Steaming

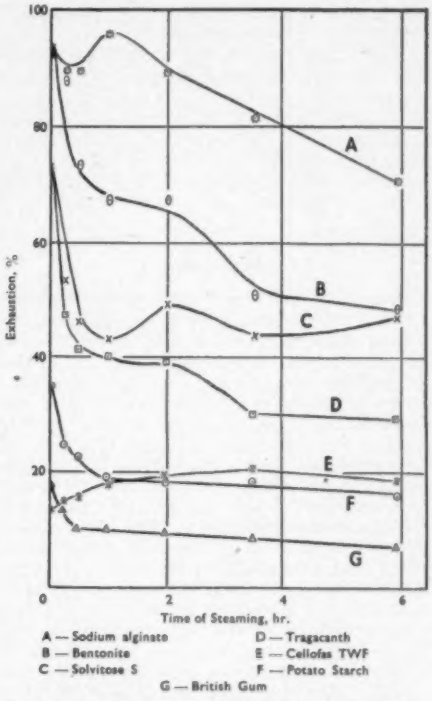



FIG. 14—Transfer of Indigosol O4B from Layers of the Pastes of Different Thickeners to Cellulose on Drying at Room Temperature and then Steaming

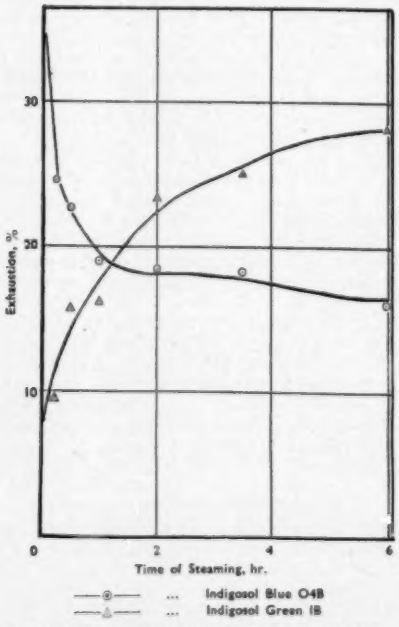



FIG. 13—Examples of Transfer of Indigosols from Layers of Starch Paste to Cellulose on Drying at Room Temperature and subsequently Steaming

Changes in the solubility of the dye, salting-on effects where there is chemical combination with cellulose or starch, and changes brought about in the distribution of water between the two phases also may have to be taken into account. With assistants like Solution Salt B and other salts of aromatic sulphonic acids, any marked inhibition of the decomposition of the Indigosol is not to be expected, and an explanation of the effect of the assistant on the exhaustion of any particular dye must be sought principally in the manner in which it can modify the respective solubilities of the undecomposed and the decomposed forms.

The hypothesis which connects the existence of more than one maximum in the exhaustion–time curves of the Indigosols with partial decomposition of the dye as a result of steaming has been tested with Indigosol Blue O4B and Cibantine Brilliant Pink R by steaming alone the film of starch containing the dye, then attaching it to the film of cellulose, and inducing dye transfer by further steaming (Fig. 10–12). Other experiments, in which transfer of the dye is effected in the cold, by drying down a layer of dye-containing paste in contact with Cellophane, give results which allow the picture to be amplified, showing what takes place when there is little opportunity for heat-induced decomposition of the original dye (Fig. 13). On the whole, the hypothesis is supported.

### EFFECT OF THICKENING AGENT ON INDIGOSOL EXHAUSTION

Munshi and Turner [1] and Reilly and Turner [5] were able to show that the course and extent of dye transfer of direct dyes between the thickener and the cellulose phases could be profoundly altered by the choice of thickener used. This has been found to be true for Indigosol Blue O4B also. The results of a series of experiments with this dye and different thickeners are shown graphically in Fig. 14.

## Discussion

### THEORY OF DIFFUSION WITH DECOMPOSITION

In the theory outlined in the Introduction, the general characteristics of the dye exhaustion curves for Indigosols are explained as arising from the simultaneous operation of two processes—(*a*) the migration of dye molecules, with a comparatively low chemical affinity, between the water contained in the respective phases, thickener and fibre substance, under the influence of changing concentration differences; (*b*) the progressive decomposition of the Indigosol by heat, with consequent modification of its diffusion properties. This theory is now discussed in greater detail. Valkó [6] has estimated that the particle size of an Indigosol at normal dyebath concentration is of the same order of magnitude as that of the sodium leuco compound of the corresponding vat dye. Rose [7] has confirmed this and shown that the Indigosols in solution can penetrate cellulose sheet rapidly. Michie, Fowler, and Vickerstaff [8] have recently suggested that sodium leuco compounds of vat dyes are intrinsically very soluble and would be molecularly dispersed over a wide range of concentration were it not for the high concentration of electrolyte which normally accompanies them in solution. Schaeffer [9] states that Indigosols from many indigoid vat dyes (e.g. Indigosols Pink IR and Red Violet IRH) form molecular dispersions, those from anthraquinonoid vat dyes (e.g. Indigosol Green IB and Golden Yellow IGK) being more strongly aggregated. It should be remembered, in applying this evidence, that dye concentrations in a print during steaming are relatively high.

Ruggli and Stäuble [10] have investigated the dyeing behaviour of four Indigosols (Blue O, Blue O4B, Pink IR, and Green IB, corresponding respectively to indigo, tetrabromoindigo, dichlorodimethylthioindigo, and dimethoxydibenzanthrone) over the temperature range 0–100°C. The exhaustion of Indigosol Blue O is relatively high at low temperatures and diminishes as the temperature rises, with some irregularity—a small maximum—at 20–25°C. With Blue O4B the exhaustion is also high at 0°C., passes through a maximum at 25°C., and then falls. Pink IR has low general exhaustion, diminishing as the temperature rises; and Green IB has low exhaustion at 0°C., rising to a maximum at 62°C. and then falling. In each case this behaviour may be ascribed to the coincident effects of increasing dispersion and decreasing true affinity as the temperature rises. The relative importance of each factor depends on the initial degree of aggregation for the particular dye at a low temperature.

Accompanying these effects there is the possibility of decomposition of the Indigosol at the temperature of steaming. It must be admitted that quantitative evidence of the removal of sulphuric acid groups as bisulphate during steaming in starch films is not conclusive. In some cases acidity does develop but, in view of the very small quantities liberated, it is not easy to measure, and the presence of the starch and dye makes it difficult to identify the acid itself. The details of reactions by which an Indigosol is transformed to a vat dye are obscure and are being investigated, but it is, of course, certain that in the complete transformation sulphate groups are lost. They may not, however, be recovered intact, i.e. the removal is not necessarily to be regarded as a normal hydrolysis. It is not unreasonable to assume that an intermediate product can exist in which one sulphate group has been removed from the Indigosol molecule, or that, alternatively, association compounds are formed between molecules of liberated vat dye and unchanged Indigosol molecules. In either case it may be expected that the product which is then formed, and which is a unit in the diffusion process, will be less soluble than the original Indigosol. Accordingly, the resultant behaviour will depend both upon the initial solubility of the particular Indigosol and upon its chemical stability in steam.

For a dye which is initially soluble a considerable transfer of Indigosol, following the acid dye pattern, will take place in the early stages (Fig. 9, Curve I). Later, a proportion of the dye in both phases may be expected to be transformed into a less readily soluble modification, leaving the remaining unchanged Indigosol to adjust itself to the new water distribution. The modified dye, either because of larger particle size, increased affinity for the cellulose and starch, or lower attraction for water, will then tend to distribute itself according to the changed water distribution either more slowly or less completely, and so its exhaustion curve will be different (Curve II). It is interesting to note that the two kinds of exhaustion curve have actually been found among acid dyes. The rapidly diffusing Naphthalene Red EAS or Scarlet R, both low in the Meitner series (i.e. of low aggregation), have curves resembling I (Fig. 9). Coomassie Brilliant Blue FF, which is higher in the Meitner series, has a curve resembling II. The overall transfer behaviour will therefore be a summation of these two, with an adjustment for the changing proportions of the compounds I and II present in the whole system as steaming progresses.

### FURTHER TESTS OF THE THEORY

If the above assumptions are essentially correct, it follows that, in experiments in which the heat-induced decomposition of the Indigosol occurs before there is an opportunity of migration to cellulose, there should be a modification in the transfer behaviour when migration is, at length, allowed to take place. This has been tested with

three different sets of conditions. A normal starch film containing Indigosol O4B was steamed for 1 hr. and then allowed to dry before being attached to cellulose and subjected to further steaming. The results are given in Fig. 10 (Curve II) in comparison with the normal transfer behaviour of the Indigosol (Curve I). It will be seen that the prior steaming treatment appears to have raised the initial exhaustion. This then decreases, and later increases as steaming in contact with cellulose continues. Allowing for the fact that some transfer would have occurred during the first hour in the normal experiment, it will be seen that, if curve II is displaced by 1 hr. along the time axis, its contours do bear a rough correspondence with the contours of I, the ordinary exhaustion curve, over the common time range.

If a solution of Indigosol O4B is heated, the containing vessel being placed in the steamer for 1 hr., before using it to make a starch paste and preparing therefrom a starch film, the exhaustion properties when this film is steamed in contact with cellulose are represented by Curve III. These results are rather more directly in accordance with the predictions of the theory, since the formation of the maximum is delayed by the steaming pretreatment. It must be remembered that factors other than decomposition of the Indigosol can influence the results when the steaming pretreatment is applied to the dye-containing film; e.g. the dye may be stabilised to some extent by the starch, and, also, the steaming may modify the structure of the starch film, changing its capacity for swelling in steam during the second stage of the experiment.

As an added test of the theory, a similar series of experiments was carried out using Indigosol O4B, this time in the presence of sodium carbonate as a stabiliser against heat decomposition. It will be seen from Fig. 11 that the steaming pretreatment has caused much less change in the migration characteristics of the dye, and it seems fair to deduce that this is because less heat-induced change has taken place.

Prior steaming of the dye-containing film was also performed with Cibantine Brilliant Pink R, the results being shown in Fig. 12. In this case, however, after steaming the film alone, it was extracted with ethyl alcohol before combining with the cellulose film and further steaming. The object of this was to extract the unchanged Indigosol preferentially, so that the subsequent transfer behaviour should represent more exclusively that of the modified form. As will be seen, initial exhaustion was again enhanced. Thereafter the curve is very complex, the effect of steaming in increasing the affinity for cellulose being again demonstrated.

### DYE TRANSFER IN DRIED-ON FILMS

Another interesting aspect of dye transfer is illustrated when a modification is made in the preparation of Indigosol–starch–cellulose systems for steaming. In this case, instead of preparing a solid dye-containing starch film for attachment to the cellulose, the starch is made into a paste, the dye is added, and a uniform layer of the wet paste is spread upon the surface of a film of cellulose, the two being dried together at room temperature for some 12–18 hr. in a circulated atmosphere of 73% R.H. As with the acid dyes, the increasing concentration of the dye in the starch layer during drying results in the transfer of appreciable proportions of dye to the Cellophane. Steaming of the combined film then causes a redistribution of the dye between the two phases. Results for Indigosol O4B and for Indigosol Green IB are shown in Fig. 13. It will be seen that a very considerable exhaustion of the dye from the starch during drying takes place with Blue O4B. When steaming commences there is a rapid return of dye to the starch, presumably because the dye molecules are not attached strongly to the cellulose by chemical bonds; the steam causes greater relative uptake of water by the starch, and the dye diffuses back into this water in an attempt to maintain the concentration. With Green IB, forward migration on drying down is less pronounced, either because the dye has a marked affinity for starch or because it is more strongly aggregated and cannot diffuse readily into the cellulose. On steaming, forward transfer to the cellulose takes place, either through disaggregation of the dye at the higher temperature or because the combination of the dye with the starch is broken and more of it can diffuse. These results are in qualitative agreement with those of Ruggli and Stäuble [10] referred to earlier in the discussion.

### TRANSFER BEHAVIOUR OF INDIVIDUAL DYES

In addition to the above discussion of examples illustrating the general theory, the following notes upon the behaviour of individual dyes are now given. Each of the dyes has been rendered as free as possible from accompanying electrolyte.

INDIGOSOL GREEN IB (Fig. 2)— Only one maximum is found in the exhaustion curve, although towards the end of the steaming period it passes through a minimum and commences again to rise. This rise might have continued further had not extensive breakdown of the starch set in. This curve is interpreted as showing that the dye is comparatively stable at steaming temperature and behaves rather like a single acid dye. The dark colour of the Indigosol in the film makes it difficult to detect incipient decomposition by observation of a change in the appearance.

CIBANTINE BROWN G (Fig. 7)— The migration behaviour appears similar to that of Indigosol Green IB, and a similar argument would apply. Here, however, some change in colour is seen as the steaming continues.

INDIGOSOL BLUE O4B (Fig. 3)— This was the first dye in which a double-peaked exhaustion curve was seen, and although the second peak is not very pronounced, its reality has been confirmed by several repetitions of the experiment. The form of the curve may be interpreted as showing that the decomposition is not extensive and that the migration rates of the normal and partly decomposed forms are not very different. This has already been discussed in the section on

steaming pretreatments. The dye must be very mobile in the first instance, since exhaustion reaches 20% on short contact of the dye-containing starch film with water-soaked Cellophane in the cold.

CIBANTINE BRILLIANT ORANGE RK (Fig. 6)—Here there is a sharply defined and very rapidly formed peak in the exhaustion curve. Transfer on contact of the two films without steaming is negligible. This is interesting, since the dye is not very soluble in cold water, and it must be taken that rise in temperature readily causes the breakdown of molecular aggregates of the dye. The presence of a second peak and the rise towards a third suggest that a number of modified forms are possible, each capable of some diffusion but at markedly different rates.

CIBANTINE BRILLIANT PINK R (Fig. 5)—This dye is interesting in that the secondary peak is very much higher than the primary one. Further, there is very marked exhaustion on contact before steaming, although the dye is not very soluble at ordinary temperatures. Colour changes during steaming give evidence of decomposition. The dye at ordinary temperatures may have an unusual range of polydispersity. These results should be considered in conjunction with the behaviour in the presence of alkali and Solution Salt B, to be discussed later.

INDIGOSOL GOLDEN YELLOW IGK (Fig. 4)—The exhaustion curve of this dye suggests that it has migration properties intermediate between those of Indigosol Green IB and those of Indigosol Blue O4B.

### EFFECTS OF SODIUM CARBONATE AND OF SOLUTION SALT B

The effects of these two assistants are discussed together, the appropriate exhaustion curves being shown, alongside those for the dyes alone, in Fig. 2–7. It will be seen that, while neither of these assistants changes the broad essential features of the exhaustion curves for any of the Indigosols, they can both bring about great alteration in detail. The relative heights and the times of occurrence of the primary and secondary maxima may be greatly modified. Both assistants tend to delay the formation of the primary peak.

There are certain consistent features in the effect of sodium carbonate on the different dyes. When the transfer on initial contact, without steaming, is marked for the dye unaccompanied by electrolyte, sodium carbonate always diminishes such transfer (Fig. 3 and 5). When the dye is relatively insoluble in water at ordinary temperatures, the carbonate seems to act fairly consistently in lowering the height of the early part of the exhaustion curve. Where it is possible, by means of a change in colour, to detect decomposition of the Indigosol during steaming, it is found that the presence of the alkali removes or greatly diminishes the evidence of this decomposition.

There are likely to be a number of factors which contribute, in greater or less degree, to the total effect of the carbonate, including—(*a*) prevention of the removal of combined sulphate groups from the Indigosol molecule at the temperature of steaming; (*b*) suppression of the hydrolysis of the ester salt—

$$R{\cdot}SO_4Na + H_2O \rightarrow R{\cdot}SO_4H + NaOH$$

leading, if relatively small additions are made, to some increase in solubility of the dye; and (*c*) increase in the proportion of water taken up by the system as an osmotic effect, the starch phase, being more readily swollen than the cellulose, thus increasing its content of water relative to the latter. On the general theory which has been put forward, effect (*a*) may be expected to suppress the second peak either absolutely or in relation to the first, making the system approach that of an acid dye in behaviour. Outstanding examples are Cibantine Brilliant Pink R (Fig. 5) and Cibantine Brilliant Orange RK (Fig. 6). Effect (*b*) may, as noted, cause an increase, perhaps not large since the Indigosols are salts of relatively strong acids, in the solubility of the dye. If the Indigosol is initially sparingly soluble, this action may increase the transfer in the early stages of steaming, e.g. Indigosol Golden Yellow IGK (Fig. 4), Indigosol Blue O4B (Fig. 3), and Cibantine Brilliant Pink R (Fig. 5).

The effect of factor (*c*) is difficult to predict in the absence of more detailed experiments. If most of the extra water acquired can be regarded as available for dissolving dye, this dye would then be retained preferentially in the starch film, as suggested by results with very soluble acid dyes, with Indigosol Green IB (Fig. 2), and with Cibantine Brown G (Fig. 7). In view, however, of the relatively high concentration of the salt if even small amounts are added to the small volume of the printing system, it should in general decrease the solubility in both phases and by aggregating the dye render initial migration slower, as exemplified again by Indigosol Green IB, Cibantine Brown G, and Cibantine Brilliant Orange RK (Fig. 6). If there is any marked affinity of cellulose for the dye, of the type found in direct cotton dyes or sodium leuco vat dyes, some "salting-on" may occur owing to the suppression of electrostatic and osmotic effects. There is little consistent evidence of this in the dyes examined, although the addition of sodium chloride has been found to cause a marked increase in the exhaustion of Indigosol Green IB. All that can be said at this stage, therefore, is that the total effect of sodium carbonate additions will depend upon a complex balance of factors which vary in relative magnitude from dye to dye.

Solution Salt B, sodium *N*-benzylsulphanilate, is used primarily as a dispersing agent for, *inter alia*, difficultly soluble leuco vat compounds and Indigosols when high concentrations must be used. This applies especially to printing applications. Together with the related sodium *NN*-dibenzylsulphanilate (Solution Salt SV) and salts of other aromatic sulphonic acids it is used especially in printing pastes for styles in which the electrolyte content of the paste must necessarily be high. As appears reasonable from the previous discussion, work by Lichtenstein [11] and Peters [12] on vat dyes

shows that the dispersing effect of these compounds must be regulated, as an excess will cause the yield to be poor. Their use is not indicated when the thickener itself acts as a dispersing agent, e.g. dextrin as opposed to starch. For the purpose of this argument it may be most accurate to regard them as dispersing agents which do not inhibit heat-induced decomposition of the Indigosol. As the partly desulphated form is assumed to be less soluble, the general theory would suggest that agents of this kind would modify, in particular, the relative height and position of the second peak, but that they could also increase the height of the first peak for dyes which are sparingly soluble. If the action is regarded as association between aromatic nuclei in the dye and the Solution Salt respectively, the agent in effect puts back the sulphate group which has been lost by decomposition.

There are some striking examples of the enhancement of transfer, particularly with Indigosol Brilliant Pink R (Fig. 5), where, presumably, the low initial solubility of the dye is overcome, and the two forms are both rendered so mobile that the two peaks on the exhaustion curve for the dye alone are suppressed and are replaced by a single broad and high peak. The transfer of Indigosol Green IB (Fig. 2) is much increased by the Solution Salt and, in a similar way though to a less extent, by the parent unsubstituted compound, sodium sulphanilate (not shown). On the other hand, the single peak in the exhaustion curve of Cibantine Brown G (Fig. 7) is flattened slightly by Solution Salt B. With Indigosol Golden Yellow IGK (Fig. 4) the primary and secondary peaks, which are scarcely evident in the exhaustion curve for the dye alone, are both greatly enhanced, the secondary peak more than the primary.

It has been suggested that, where removal of combined sulphate groups causes the solubility of the Indigosol to be substantially diminished, with a corresponding decrease in the mobility of the dye molecules, the addition of Solution Salt B will cause the secondary peak to be enhanced in relation to the primary. This is supported most strongly by the exhaustion curves for Cibantine Brilliant Orange RK and Indigosol Blue O4B (Fig. 6 and 3). It would not be safe to assume that this simple mechanism represents all the possibilities, for, in a comparable series of experiments with Indigosol Blue O4B, using respectively sodium *o*-toluidine-sulphonate and trisodium naphthalenetri-sulphonate in place of Solution Salt B, it is the primary peak and not the secondary which is enhanced. Differences of this kind may be caused by steric or other factors which influence the association of the dispersing agent preferentially with either the unchanged or the partly decomposed form of the individual Indigosols. The effect of other dispersing agents, with quite different constitutions from Solution Salt B, seems also to be specific. For instance, addition of Butyl Cellosolve (Gen. Met. Chem.) (ethylene glycol monobutyl ether) to Cibantine Brilliant Pink R changes the exhaustion curve with its low broad primary peak and its higher broad secondary one to a curve with a rapidly formed, narrow, high, primary peak, a broader secondary one of the same height, and evidence of the possible formation of a third if the steaming could be continued for a sufficiently long time. Urea retards the formation of the normal sharp primary peak of Cibantine Brilliant Orange RK and broadens it markedly.

It is obvious, therefore, that the migration behaviour of the Indigosols is complex, that the influence of some of the common printing assistants is specific to the individual dyes, and that a much more complete investigation of a larger range of dyes is necessary before a full understanding of this behaviour can be attained.

### TRANSFER BEHAVIOUR OF SOLEDON BLUE RCS

This dye forms one of the very small group of anthraquinonoid Indigosols having four combined sulphate groups. With four strongly polar groups it is very soluble in water. It loses combined sulphuric acid if the pH of the solution falls below 7, the loss being marked by a series of colour changes from brownish yellow and violet to blue as the solution becomes more acid. With this decomposition the solubility in water diminishes and the affinity for cellulose rises [13]. Because of this instability it is impossible to use it for transfer experiments after the stabilising alkali is removed, and therefore the commercial form of Soledon Blue RCS has been investigated without any attempt at the removal of accompanying electrolytes. The parent dye is itself liable to oxidise from reduced forms to stages beyond the normal diquinone, giving products greener in colour, and this has been variously ascribed to transformation into azines [14,15]. Oxanthrone formation has also been reported [15,16].

The exhaustion curve given in Fig. 8 shows that the transfer from the starch film on contact before steaming is considerable (47%). On steaming there is a slight drop, and then a high narrow peak is formed, followed by a slow secondary fall and rise. It will thus be seen that high exhaustions are obtained accompanied by considerable mobility of the dye molecules. Even with an excess of added sodium carbonate (equal in weight to the commercial dye product) colour changes take place. Up to 1 hr. in the steam little change is seen, from 1 to 2 hr. the colour is claret, and from 2 to 6 hr. it goes to dark brown. Parallel changes do not take place at 100°C. in aqueous solutions containing similar proportions of carbonate. Changes in pH seem more pronounced in the starch film than in the solution, and this may be due to the greater concentration in the film, leading to a greater effect from acid liberated from the dye in the initial stages.

Soledon Blue RCS may well, on further investigation, illustrate the operation of two very different, and at first sight paradoxical, causes of dye transfer from starch to cellulose. If the dye has a true affinity for cellulose, i.e. if its molecules can combine with fibre molecules through chemical bonds, then the presence of a large proportion of $-SO_4Na$ groups in the molecule will tend to keep the dye in the dyebath and lower the exhaustion.

The loss of some of these groups should then increase retention by the fibre. Thus at the end of the steaming period much of the Soledon Blue 2RCS found in the fibre substance may be retained there through this cause. On the other hand, in a printing system, where dye is present initially at high concentration in the thickener film and can diffuse substantially without adsorption under a concentration gradient into the cellulose, the presence of a large number of combined sulphuric acid groups in the cellulose, rendering it very soluble in water and combating molecular aggregation, can increase the mobility and facilitate the transfer by a mechanism similar to that postulated for the highly soluble acid dyes. This factor may account for the high and rapid exhaustion of dye on first bringing dye-containing starch film and water-soaked cellulose together before steaming commences. The loss of sulphuric acid groups can then explain the rising tendency of the curve in the later stages of steaming.

#### EFFECTS OF RELATIVE CHANGES IN CONCENTRATION AND RELATIVE CHANGES IN VOLUME IN THE TWO PHASES

With Indigosol Blue O4B as the dye, experiments have been made in which the relative weights and volumes of the thickener and cellulose phases, with a constant area of contact, have been varied. In the first case the thickness of the starch film and the initial concentration of dye within it have both been maintained constant, but two grades of Cellophane, 300 PT and 600 PT, have been used. The latter grade is twice as thick as the former. The essential shape of the exhaustion curve on steaming is unchanged, but the exhaustion is uniformly higher with the thicker Cellophane. Initial exhaustion before steaming rises from 20·4% to 28·5%, and exhaustion at the primary maximum from 24·3% to 37·2%. Similarly, keeping the thickness of the Cellophane constant (300 PT) and using two thicknesses of starch film (0·004 in. and 0·0085 in. measured on the dry film) with the same initial dye concentration, the initial exhaustion drops from 20·4% to 8·2% and the exhaustion at the primary peak from 24·3% to 10·6%. For this dye, therefore, the original postulate for soluble non-substantive acid dyes, viz. that the dye will tend to distribute itself between the two phases in a direct relation to the free water content of each, seems to apply.

#### EFFECT OF DIFFERENT THICKENERS ON EXHAUSTION

The results of these experiments are shown in Fig. 14. In view of the difficulty of making solid films of some of the thickening agents, the technique, already described, was adopted whereby the wet dye paste was spread to a standard uniform thickness on the Cellophane before drying down at room temperature. After drying, the double film was steamed. Blue O4B was used as a typical Indigosol, and it is seen that a considerable exhaustion occurs on drying down. Except with Cellofas TWF (cellulose carboxymethyl ether) migration back to the thickener takes place on steaming. Detailed comment is reserved until further work has been done, but it will be seen that the results obtained by Reilly and Turner [5] for direct dyes do not, on the whole, contradict the present results, high exhaustion being obtained with sodium alginate and with the chemically inert thickener bentonite.

## Experimental

#### PREPARATION OF DYE-CONTAINING FILMS, ADHESION, AND STEAMING

The technique devised by Munshi and Turner [1] and by Reilly and Turner [5] has been adopted without essential modification, and calls for little further description. In making the printing paste, spreading, drying, and steaming, care was necessary when working with Indigosols to exclude light from the system as much as possible. Supplies of Indigosol and Cibantine dyes were furnished respectively by Messrs. Durand & Huguenin and Ciba Ltd. These were purified to contain as little electrolyte as the limited stability of the products would allow; they were delivered and used with no unnecessary delay. When they had to be stored, this was done in a refrigerator with the complete exclusion of light. Except when stated otherwise, potato starch was used as the thickening agent. In general, the initial dye content of a unit disc was 1·5–2·5 mg. expressed as weight of parent vat dye.

#### DEVELOPMENT OF THE INDIGOSOL

After the Indigosol-containing film had been combined, in the usual way, with soaked Cellophane (normally 300 PT grade used after repeated washing), an operation which required 2–3 min., steaming was carried out for the desired time. Immediately on removal from the steamer, the Indigosol in the system was transformed into the corresponding vat dye by treatment for 1 min. with dilute nitrous acid (equal volumes of a cold solution of sodium nitrite (15 g./litre) and sulphuric acid (20 ml. conc. acid per litre at 90°C.)). Washing in several changes of water followed. Experiments in which quinol (7·5 g./litre) was added to the acid solution caused negligible increase in the yield of vat dye from a given amount of Indigosol on development, and it was concluded that destructive oxidation of the dye at this stage could be disregarded.

In every series of transfer experiments, some were included in which, immediately after the starch and cellulose films had been brought firmly into contact, the combined films were developed, and a measurement made of the dye which had been transferred to the cellulose during this very short period of contact in the cold. This transfer, which, as already noted, was sometimes considerable, is shown in the curves as exhaustion at zero steaming time.

#### ESTIMATION OF DYE IN STARCH AND CELLULOSE

Because of the very feeble colour of many of the Indigosols, together with the possibility of decomposition during steaming and extraction, the dye was invariably transformed, as described above,

into the parent vat dye before colorimetric estimation. For similar reasons, no attempt was made to calibrate the cut discs of starch film for initial dye content by the method of Munshi and Turner [1]. Instead, these discs were used as obtained, and the exhaustion after steaming and development was determined by direct estimation of the dye content of the separated starch and cellulose phases respectively. This method allowed also, within the limits of experimental error (approx. ± 2% among single determinations), an estimate to be made of possible change in total dye content of the system through destruction during steaming. No positive evidence of this destruction has been found for any of the Indigosols examined.

The removal of the developed vat dye from the separate starch and cellulose films, by solvent extraction prior to colorimetric measurement, presented some difficulty. The dimethoxydibenzanthrone from Indigosol Green IB could be removed from each kind of film by repeated extraction with cold redistilled pyridine over a period of two days, and this method gave satisfactory results. The tetrabromoindigo from Indigosol O4B is decolorised by long standing with pyridine, and the colour could not be made to return by the addition of a variety of oxidising and reducing agents. After many organic solvents had been tested, without satisfactory result, the method of Guelke and Fitzsimons [17] was adopted with some modification. In this method, which was found to be applicable to dyed starch also, dyeings of vat dyes are dissolved in cold concentrated sulphuric acid. Pure acid is essential, since traces of metallic impurity can have disturbing effects on the colour of the dye when in solution. With some of the vat dyes, especially when they are dissolved in the presence of starch, the colour of the sulphuric acid solution continues to change slowly in intensity for several hours after it has been prepared, and before a reliable colorimeter reading could be obtained it was necessary to allow the solution to stand in a cool dark place for some time. A standard time of 44 hr. was finally employed. The following procedure was at length adopted. The specimen was removed from the steamer and developed. The starch film was peeled off and supported on a fresh slip of Cellophane. This, along with the original strip of Cellophane containing printed circles $\frac{11}{16}$ in. in diameter, was allowed to dry in the air for 18 hr. The Cellophane was cut so that each printed circle or each disc of separated starch film was carried on a piece 1 in. square. This square was dissolved in an accurately measured volume (usually 25 ml.) of cold concentrated sulphuric acid in a tube of resistance glass, stirring with a glass rod being continued until complete solution had been obtained. The tube was closed and allowed to stand in the dark for the standard time. When measuring the dye on cellulose, a comparison solution for use in the Spekker was made by dissolving 1 sq. in. of undyed Cellophane in the necessary volume of acid. For determination of dye in starch, the comparison solution was made by dissolving 1 sq. in. of Cellophane and one standard disc of undyed starch film. The Spekker was calibrated with a series of standard solutions of the appropriate pure vat dye in sulphuric acid.

Where additions, such as sodium *o*-toluidinesulphonate, contributed to the colour of the sulphuric acid solution, this contribution was estimated in experiments in which the migration of the assistant was allowed to take place in the absence of dye, and its separate effect thus determined. The gross value for the exhaustion of the dye in the presence of the agent could then be corrected, and a net value for the dye alone obtained.

* * * *

We desire to express our thanks to Messrs. Durand & Huguenin A.-G. (through Bard & Wishart Ltd.), Ciba Ltd., Clayton Aniline Co. Ltd., and Imperial Chemical Industries Ltd. for specially prepared dyes and other chemicals and for information and advice which greatly facilitated the investigation.

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## Discussion

**Mr. W. Clarke**: The difficulty of producing dyes of the leuco vat ester type absolutely free from electrolyte is well known. In view of the fact that the theory put forward to explain the transfer mechanism is essentially diffusion with decomposition, have the authors considered the possibility that insidious decomposition of the dye powder might have occurred during storage? It is not inconceivable that the rate of decomposition of the purified Indigosols may vary from dye to dye during storage, and that a partly decomposed sample might show anomalous transfer behaviour. Have the authors attempted to ascertain, by conducting accelerated storage tests on the Indigosol

powders, that their stability is such that their behaviour may reasonably be assumed constant throughout the period of the experiments?

Mr. TURNER: The precautions suggested may well be called for when this work develops. The feature of instability was recognised, and the samples of dye with reduced electrolyte, particularly carbonate, content had been sent over by air mail and were used as soon as possible. Some of the indigoid members of the series may be purified by crystallisation, but not all Indigosols can be dealt with in this way. The results given in the paper show that, in what must be regarded as a preliminary survey of the problem, we have taken the effect of heat into account. Apart from this, the known behaviour of Indigosols suggests that it would be dangerous to regard a short time of storage at a high temperature as equivalent to a longer time at a lower temperature in its effect upon decomposition. This is what accelerated decomposition tests would have to rely on.

Mr. A. S. FERN: The curve showing rate of transfer of Indigosol Golden Yellow IGK in presence of Solution Salt B (Fig. 4) has two maxima, two minima, and five points of inflexion (since an equilibrium state must also be reached). What occurs in the transfer process to account for each point of inflexion?

Mr. TURNER: The transfer phenomena of acid dyes on which the theory of simultaneous migration and decomposition is based have not been brought out very strongly in this presentation because the time allowed is short. We are not entirely happy about the theory put forward for the acid dyes themselves. Some of the discrepancies are pointed out in a paper which has been submitted recently for publication in the *Journal*. In the meantime, Mr. Pomfret is endeavouring to define the changes in water content in the starch–cellulose system with greater precision, since we feel that part of the secret lies there. In the example quoted, the number of inflexions in the exhaustion curve are too great to be explained by the simple theory, but the association between either undecomposed or decomposed Indigosol molecules and Solution Salt B could very easily be quite a complex process. We have no experimental results beyond those given by which this behaviour could be defined.

Dr. G. LANDELLS: In the dye transfer experiments in which urea has been used, is it possible to deduce from the graphs obtained the mode of action of the urea?

Mr. TURNER: Three modes of action seem to be possible, all of which could have a substantial effect upon the course of transfer— (*a*) Swelling of the starch with increase in its water content; this would tend to encourage dye to stay out of the cellulose. (*b*) Swelling of the cellulose itself; this would encourage the exhaustion. (*c*) Increase in the dispersion of the dye particles; this would have different results on the transfer according to the dispersibility of the particular dye or particular form of dye in water alone. With acid dyes we have had results which suggest that (*a*) is most important when the tendency of the dye towards aggregation is low; (*b*) and (*c*) are more important when it is high.

Mr. R. L. HILL: In view of the prolonged steaming used in the experiments, is it not possible that modification of the starch films occurs, particularly when sodium carbonate is present. It is especially interesting to note that curves for potato starch and British Gum in Fig. 14 do not exhibit the characteristic double-peaked curve for Indigosols.

Mr. TURNER: It is not possible to decide this point by the comparison suggested, since, as explained, the results in Fig. 14 come from a drying-on technique, while the double-peak effects are obtained by using a solid starch film. Nevertheless, the information we have inevitably suggests modification, since ultimately the starch begins to run. We are seeking information as to whether liquefaction or the stage before liquefaction corresponds to a large proportionate rise in the water content. Carbonate helps this effect, as we have found in experiments with vat dyes in which potassium carbonate is present in the film.

# The Use of Acetate Rayon Dyes in Textile Printing

W. Shaw

Means of printing acetate rayon dyes on to cellulose acetate, nylon, and other synthetic fibres are discussed. The difficulties associated with the production of satisfactory discharge prints on acetate rayon and nylon coloured with these dyes are detailed, and methods proposed to overcome them are reviewed.

## INTRODUCTION

The commercial production of cellulose acetate rayon was begun shortly after the end of the first world war, but the new fibre soon encountered a serious threat to its development in the lack of affinity that it exhibited for the great majority of dyes known at that time. An extensive survey of the various dye classes enabled a heterogeneous range of dyes for acetate rayon to be assembled, but this was by no means satisfactory for dyeing, and still less so for printing. The possibility of partly hydrolysing cellulose acetate so as to impart to it an affinity for the dyes normally used for dyeing cellulosic materials had already been recognised for some time, but the loss in weight and strength of the fabric which occurred, together with processing difficulties encountered in certain cases, prevented the general application of this process. In view of this position a search for new dyes with a strong affinity for cellulose acetate was begun by the British Dyestuffs Corpn. Ltd. (B.D.C.) and by British Celanese Ltd., which resulted first in the discovery of the Ionamine (BDC) type of water-soluble acetate dyes, followed by that of the Duranol (ICI) and S.R.A. (BrC) disperse dyes.

The Ionamines, which are now obsolete, were prepared from insoluble aminoazo or aminoanthraquinone compounds possessing an affinity for acetate rayon by the introduction of an *N*-sulphomethyl group[1, 2]. The dyes obtained in this way are soluble in cold or slightly warmed water, but decompose slowly in a hot dyebath, or during steaming in the case of prints, to regenerate the insoluble base in a finely divided form, easily absorbed by the fibre.

The disperse acetate dyes, which were independently discovered by Baddiley and Shepherdson of B.D.C. and by Holland Ellis of British Celanese Ltd., are still by far the most important class of acetate dyes at the present time. The S.R.A. dyes of the latter firm initially consisted of fine dispersions of amino- or hydroxy-azo compounds produced with the aid of sulphoricinoleic acid as a dispersing agent, while the former company marketed dispersions of aminoanthraquinones under the name of Duranol dyes. Since that time many improvements have been effected in both the colouring matters and the methods of dispersion employed, while a number of other dyemakers have also introduced ranges of disperse acetate dyes.

Water-soluble dyes with an affinity for acetate rayon, differing from the Ionamines in that they are stable in the dyebath, were marketed by Imperial Chemical Industries Ltd. in 1936 under the trade name of Solacet dyes, their preparation being based on the discovery that a sulphuric ester group, such as the sulphuric ester of an azo dye containing an *N*-$\beta$-hydroxyalkyl group, imparts water solubility without destroying the affinity of the dye for cellulose acetate[3]. Other methods of producing soluble dyes with an affinity for cellulose acetate have since been devised, but so far the Solacets constitute the only range of this type of colouring matter in general use.

Just before the last war the I.G. marketed a new range of water-soluble dyes for printing cellulose acetate entitled Astrazon dyes. These belong to the basic class, but are said to be of better light fastness than the older triphenylmethane type previously used in dyeing[3]. Little or no experience has been obtained of the application of these dyes in practice, but small-scale tests indicate that certain members of the range may be of interest, because of their brightness, when supplies become available.

The advent in recent years of new synthetic fibres such as nylon, Terylene, and Orlon has provided fresh uses for both the disperse and water-soluble acetate dyes in dyeing and printing these materials, the disperse acetate type especially being more generally applicable than any other class of dyes in the coloration of these hydrophobic fibres.

## GENERAL CONSIDERATIONS IN REGARD TO PRINTING

It is well known that certain members of the disperse acetate series of dyes are unsuitable for use in printing because of their tendency to sublime during the steaming process, a feature that can give rise to marking-off troubles and cause a loss in sharpness of the printing mark. It is necessary, therefore, to select for printing only those dyes that do not exhibit this property. In spite of this restriction of choice, however, an adequate range of colours is available for many printing uses. No such selection is required in the case of the Solacets, which are all non-volatile, while the Astrazon dyes also are said to be satisfactory in this respect. It is of interest, however, to note that samples of fabrics printed with the latter dyes were examined by a B.I.O.S. Textile Mission to Germany, when marking off was observed, presumably due to volatilisation of the dyes under the conditions of storage[4].

Whenever possible, the disperse acetate dyes are used in paste form rather than in the form of powders for printing purposes, their disadvantages from the point of view of storage being far more than counterbalanced by the advantages derived

from their fine state of dispersion, which makes the preparation of printing pastes easy and rapid, and in many cases leads to more level prints and a greater colour yield than can be obtained from the same dyes in powder form.

A wide range of printing thickenings is available, the disperse acetate and Solacet dyes being compatible with all those in general use. It is essential, however, to employ a thickening that can be easily removed during the washing-off process, even under the mild conditions customarily used for acetate rayon dyes printed on acetate rayon and nylon fabrics, while care must also be taken to select one that does not cause reaggregation of disperse dyes. Furthermore, it is desirable to use a thickening of high solid content in printing fabrics of a hydrophobic nature, in order to obtain level prints with a sharp mark, even though this results in rather lower colour yields. Usually a type of gum arabic is employed for printing acetate dyes with very satisfactory results, but where difficulty in penetration is experienced, or there is a danger of mechanical damage with very delicate fabrics, gum tragacanth or locust bean thickenings are suitable alternatives. Oil-in-water emulsions have been proposed as vehicles for the printing of cellulose acetate rayon with acetate dyes[5] and, providing a satisfactory printing mark can be obtained, should be superior to gum-thickened printing pastes, as washing after steaming is said to be unnecessary.

The preparation of printing pastes with disperse acetate rayon dyes is very simple, the dye in paste form being diluted with water and strained into the printing thickening, to which has been added any necessary assistants such as glycerol, thiodiglycol, etc. The printing colours are very stable and are not affected by the use of metal containers such as galvanised iron. When water-soluble acetate rayon dyes are to be used they are dissolved in hot water with the aid of a hydrotropic agent, generally sodium dibenzylsulphanilate, and the solution is strained into the printing thickening containing the other requisite ingredients. In cases where solution is difficult an improvement can often be achieved by the addition of small amounts of ammonia or butanol.

In machine printing it is necessary to use a finer scale of engraving, for printing acetate rayon, nylon, and other fabrics of low water absorbency, than is usual for cellulosic materials of a similar construction, so as to reduce the amount of printing colour transferred to the cloth. Even so, special allowances for flushing or spreading out of the pattern are made when engraving the printing rollers.

### PRINTING CELLULOSE ACETATE RAYON FABRICS

The disperse acetate rayon dyes suitable for printing provide a range of shades of moderate to good light fastness and of fair resistance to washing. The yellows are bright, while the orange section has recently been strengthened in this respect by the introduction of Serisol Brilliant Orange N2GD (YDC). The reds and scarlets are satisfactory, though a brighter scarlet would be acceptable, and no really bright pink of the disperse acetate rayon type is known. Bright fast-to-light shades of cerise are available, but some of the homogeneous violets are deficient in these respects, and mixture shades are to be preferred. The blues are generally good, but difficulty is experienced in building up deep royal blues of satisfactory brightness in machine printing with the disperse acetate rayon dyes alone. Some success has, however, resulted from the use of a mixture of a disperse acetate rayon blue and a chrome dye of the Gallocyanine type, applicable without any mordant. Greens, browns, and blacks are usually obtained by means of mixtures without any difficulty, though the greens are not of the highest brightness. An improvement in this respect is attainable by the use of a turquoise blue basic dye of the type of Acronol Sky Blue 3G (ICI) as a shading component of the mixture. Navies prepared from mixtures of the disperse acetate rayon dyes are somewhat lacking in brightness, and a chrome dye such as Solochrome Prune AS (ICI), printed without mordant in the presence of urea and thiodiglycol, is generally used to produce this shade. Whenever the pattern permits, Diphenyl Black is introduced for blacks, its use being desirable from the points of view of both quality and cost.

The Solacet range is not as complete as the disperse series. There is no bright cerise such as Duranol Brilliant Red X3BS (ICI) available, while Solacet Fast Blue 2B is difficult to dissolve in high concentrations and is therefore suitable only for pale and medium shades. On the other hand, a homogeneous green Solacet of good light fastness is known.

A feature of the disperse and water-soluble acetate rayon dyes that has attracted considerable attention for a number of years now is the tendency for certain blue and violet shades to fade in the presence of oxides of nitrogen. Obviously the more highly sensitive dyes, as for instance the 1:4:5:8-tetra-aminoanthraquinone type, should be avoided wherever possible, while further protection can be obtained by the use of a suitable inhibitor, the more modern types of which possess an affinity for cellulose acetate and may be included in the dyebath or printing paste[6]. So far as printers in this country are concerned, however, complaints upon the score of gas fading are exceedingly rare, even though inhibitors are not generally employed.

Very little use has been made of acetate rayon dyes for the printing of furnishing fabrics, but it is of interest to note that Egerton[7] has shown that only a very few members of the disperse or water-soluble ranges have any accelerating effect upon the photochemical degradation of cellulose acetate, although many of them do have a pronounced effect in the case of nylon.

At the present time the water-soluble acetate rayon dyes are little used for the production of print-on styles, apart from specialised applications such as the printing of pile fabrics, where the use of disperse dyes in mixtures is liable to give rise to unsatisfactory results. The disperse acetate rayon dyes are to be preferred for general printing purposes because of their greater ease of application

and their lower sensitivity to variations in steaming conditions. It is found with the Solacets that they tend in some cases to bleed in moist steam if printed in strong shades, while the use of dry steam produces a considerable decrease in colour yield. The latter effect can be greatly reduced by the inclusion of ammonium thiocyanate or urea in the printing colours.

The disperse acetate rayon dyes can be applied successfully without the addition of any solvents or swelling agents if the prints are steamed for a long period in fairly moist steam, but they do not fix quite so well if the steam is dry. Many substances have been suggested for use as printing assistants for the disperse acetate rayon dyes, such as glycerol, thiodiglycol, di- and tri-ethylene glycols, methylated spirits, ammonium thiocyanate, and urea. Very good results have been obtained in practice by means of an addition of urea, which increases the speed of colour fixation, improves the colour yield, and affords a good measure of protection against dry steaming conditions. The use in printing pastes of a wetting agent such as Perminal KB (ICI) has been found to be of assistance in the production of smooth prints on hard cloths such as tightly woven poults and taffetas.

No special technique, other than the use of finer roller engravings than are usual for cellulosic materials in machine printing, is necessary for the application of acetate rayon dyes. Bump greys are nearly always employed except in the case of very light patterns. Gum Senegal is used to gum the piece to the bump, a process that is always carried out when printing locknit fabrics, and whenever difficulty in fitting the pattern is experienced with other cloths. Normally the printed piece is separated from the bump grey immediately after it leaves the last roller in the printing machine, but in the case of locknits it is customary to leave them gummed to the bump and steam them in this state. Bumps that have been used for this purpose are quite suitable for general printing purposes after washing, but must not be used for locknits again, as sufficient of the finely dispersed acetate rayon dyes from the previous pattern is retained to cause very serious marking-off troubles during steaming.

Printing troubles with the disperse acetate rayon dyes are uncommon. No difficulty is experienced with the formation of solid colour deposits in roller engravings, and either brush or ordinary colour furnishers may be employed. Specky prints are very rarely encountered if dyes in a paste form are used in the preparation of the printing colours. The main fault that arises in practice is the scumming or facing of the fabric that is found on occasion when very strong shades, especially wines, are printed. The great majority of printing difficulties that are associated with acetate rayon printing are due to the supplementary dyes employed. When a Gallocyanine type of chrome navy is used, colours from previous printing rollers sometimes "build" on the navy roller, and eventually etching away of the copper beneath these deposits is found to occur. This difficulty may be overcome by the use of a chromium-plated roller for the navy colour. When basic dyes are present in a pattern, care must be taken to avoid the addition of anionic wetting agents to, or the use of acid dyes in, the other printing pastes present during machine printing, as "building-on" or "tailing-down" troubles can arise in both these cases.

Penetration difficulties in the case of piece-delustred fabrics are sometimes attributable to a deposit of insoluble soaps in the material, crêpes being especially prone to this defect. It is advisable, therefore, to ensure the removal of any deposits of this kind by a treatment in a solution containing a metal-sequestering agent before dyeing or printing.

The fixation of the disperse dyes on acetate rayon requires a steaming time of one hour or more at atmospheric pressure under fairly moist steaming conditions. Their sensitivity to variations in steaming conditions is not so pronounced as that of the Solacets, but a marked difference can be seen between portions of the same prints steamed at 101–102°c. and at 110°c. when no hygroscopic or swelling agents have been incorporated in the printing pastes. Care must be taken to avoid marking-off in the steamer, and steaming between greys is recommended for heavy patterns. Water spray or drops are particularly undesirable when steaming acetate rayon fabrics, as they can cause relustre marks on delustred cloths that cannot, of course, be removed. Fabrics printed with these dyes may be kept without difficulty either before or after steaming so long as they are kept dry.

Recently A. K. Saville [8] has suggested the use of increased amounts of solvents in acetate colour printing pastes for the purpose of reducing the steaming time from 1 hr. to 10 min. without loss of colour yield. A preliminary evaluation of solvents indicated a mixture of diethylene glycol and glycerol to give very good results, and also showed it to be possible to employ concentrations as high as 20% in the presence of a conventional thickener such as gum tragacanth or carboxymethyl cellulose. Large-scale trials are said to have given very satisfactory results without any flushing of the prints or loss of colour yield or fastness, and to have shown no tendering of the fabric.

British Celanese Ltd.[9] have proposed the steaming of prints of disperse acetate rayon dyes at temperatures below 100°c. in an atmosphere saturated with water vapour, either by using saturated steam at subatmospheric pressure or by using air saturated with water vapour at atmospheric pressure or slightly above it. Temperatures of 94–97°c. are preferred, and in these circumstances steaming times of 20–60 min. are said to be required. This invention is claimed to make it possible to produce good prints with a sharp outline and good penetration without the need to use costly assistants or extra processing steps, but, so far as is known, the process has not been employed in practice to any extent.

Pressure steaming is not advisable so far as acetate rayon is concerned because of the adverse

effect it can have upon the strength of the material. It has been found, for example, that a cellulose acetate fabric that had been steamed for only 3 min. at a pressure of 20 lb./sq. in. had lost over 40% of its tensile strength[10].

In washing off acetate colour prints it is desirable to wash away all the printing thickening and surplus colour with cold water, and to avoid warm soaping treatments that may cause staining of the white portions of the cloth. Acetate rayon satins and taffetas are usually washed off in an open soaper that is linked to a set of drying cylinders so as to make washing and drying a continuous process. In this case warm water is employed as a washing medium in order to ensure removal of the thickening during the comparatively brief washing period. Acetate rayon crêpes and locknit fabrics are washed off in a rope washing range with a good flow of cold water in each beck, after which they are hydroextracted and dried as soon as possible. It is essential when carrying out this process to remove all surplus dye and thickening prior to hydroextraction, or marking-off will occur.

### NYLON

The application of the disperse acetate rayon dyes to nylon by printing is carried out in very much the same way as in the case of acetate rayon. In general, the same range of dyes that is available for printing cellulose acetate is also suitable for printing nylon, no more than a slightly increased tendency to sublime during steaming being observed with the latter material. The insoluble acetate dyes are generally somewhat duller in shade on nylon than they are on cellulose acetate, the difference being particularly marked in the case of the orange and scarlet dyes, while individual dyes have been found to give different shades on the two fibres, a notable example being Dispersol Fast Orange AS (ICI). The available range of colours has recently been extended and improved by the addition of Serisol Brilliant Orange N2GD, already mentioned, which gives very similar shades on nylon to those obtained on acetate rayon, and of Serinyl Brilliant Scarlet RD (YDC), which gives brighter scarlets of fairly good light fastness on nylon than were previously obtainable from the acetate dye range. This dye also produces good scarlets on acetate rayon, but is unsuitable for use in this case because of its very poor light fastness on this fibre.

Light fastness tests[11] have shown a number of the disperse acetate rayon dyes to be somewhat inferior in this respect on nylon compared with cellulose acetate materials, the yellows, oranges, and reds showing in general a greater deterioration than the rest of the range. Even so, it is possible to select a range of printing dyes with an adequate fastness to light for the majority of purposes. It should furthermore be borne in mind that the nylon fabrics on which these tests were performed contained a small quantity of titanium dioxide, which is known to have a deleterious effect upon the fastness to light of the disperse acetate rayon dyes on this material.

The insoluble acetate dyes have a fairly satisfactory resistance to washing at 40°C. on both nylon and cellulose acetate, but are liable to cause bad staining of the whites, and to undergo a considerable loss of depth if washed at higher temperatures. This degree of washing fastness is, of course, not high enough for many textile applications, and is likely to prove a more serious obstacle to the use of this type of colouring matter on nylon than is the general light fastness of the range.

It is of interest to note that the disperse acetate dyes when applied to nylon show an advantage over corresponding colorations on acetate in their resistance to gas fume fading, the dyes that are liable to exhibit this fault being much more resistant on the former fibre.

As in the case of acetate rayon, the insoluble disperse dyes are normally printed with the aid of a thickening of high solid content, gum arabic being the usual choice, although British Gum and textile gum have also been recommended[12]. The addition of assistants, such as urea, ethylene glycol monoethyl ether, diethylene glycol, or glycerol, is of help in the production of smooth level prints, because of their dispersing and dye-solubilising effects[13], while the addition of a suitable wetting agent to the printing pastes is also of assistance in this respect.

The fixation of acetate dye prints on nylon normally requires a steaming period of an hour, but, as in the case of prints on acetate, the inclusion of large amounts of solvents in the printing pastes is said to enable fixation to be completed in ten minutes[8]. As would be anticipated, however, the use of large amounts of hygroscopic agents has been found to increase the liability of the prints to flush during steaming, and it is necessary to adjust the quantities added to suit the steaming conditions employed.

In 1949 details of a new method for the application of various types of dyes to synthetic fibres such as nylon, Terylene, and Orlon were published[14]. This procedure, which has been named the Thermosol process, is carried out by printing or padding the material with suitable dyes, and fixing them after drying, by means of a high-temperature heat treatment for a short time, when the dye appears to dissolve in the fibre. The conditions of fixation employed depend on the type of fibre being treated, and temperatures of 180–250°C. and times of 5–60 sec. are employed. The Thermosol process may be used to apply selected non-subliming acetate dyes to nylon, but as the shades tend to be duller than when applied in the normal manner, and no compensating advantages other than rapid fixation are obtained, the method is not expected to be used widely in practice.

Tests have shown the Solacet type of acetate dyes to be suitable for printing nylon fabrics and have indicated them to be less sensitive to steaming conditions on this material than when applied to acetate rayon, although it is still advisable to add urea to the printing pastes to guard against irregularities in colour fixation that might arise

from this cause. The high affinity of these dyes for nylon, together with their superiority to the disperse acetate dyes in washing fastness on this fibre, makes them attractive for printing purposes, but the lack of bright scarlets, cerises, light-fast violets, strong bright blues, satisfactory navies, and a black prevents their use as an independent range. Certain dyes should, however, be of value as supplementary dyes to the acid dye class.

### OTHER FIBRES

Acetate rayon dyes of both the disperse and water-soluble types have been suggested[15] for use in printing Terylene, with or without the aid of carriers such as phenol, *m*-cresol, $\beta$-naphthol, guanidine, aniline, dimethylformamide, benzyl alcohol, and many others. In practice the disperse acetate dyes are superior to the Solacets, which have a lower affinity and do not print well. Fixation is said to be poor without a carrier when carried out by steaming at atmospheric pressure, but is greatly improved by steaming under pressure at 10–30 lb. per sq. in., while lower pressures may be employed if a suitable carrier is incorporated in the printing colours. The disperse acetate dyes are considerably faster to washing on Terylene than they are on acetate rayon, and behave similarly on Terylene and nylon in their resistance to oxides of nitrogen. A comparison of the light fastness of this class of dyes on Terylene and cellulose acetate does not permit any generalisation to be made. Some dyes are faster on the former fabric than they are on the latter, while others show the opposite effect[16].

Disperse acetate dyes with an adequate resistance to sublimation may be applied to Terylene, or *Dacron* as it has been recently named in America, by means of the Thermosol process[14], and are said to give very good results by this method when care is taken to avoid variations in the heat-treatment temperature, which can cause variations in dye fixation. Prints of disperse acetate dyes on Terylene that had been fixed in this way were found to be of equal fastness to light, washing, and rubbing to prints fixed in the conventional manner, but to be superior to the latter in brightness and colour yield.

In addition to the disperse acetate dyes, selected vat dyes have been found to be applicable to Terylene by the Thermosol process without prior reduction, thus making it possible to use them in mixtures with the former type of dye for shading purposes.

Orlon, the new polyacrylonitrile fibre developed by E. I. du Pont de Nemours & Co., may also be printed with the disperse acetate dyes, fixation being achieved either by pressure steaming, or by steaming at atmospheric pressure in the presence of a carrier such as resorcinol. The prints are said to have a very good resistance to washing and normal light fastness, but are not of high fastness to rubbing[17].

The Thermosol process, again, may be used to fix disperse acetate dyes on Orlon, and in the two instances reported gave higher colour yields than could be obtained by pressure steaming. The prints were of better fastness to washing and rubbing, and of equal fastness to light, when compared with colours fixed by the latter process.

### DISCHARGE PRINTING ON ACETATE RAYON DYE GROUND SHADES

A number of the disperse and water-soluble acetate rayon dyes are dischargeable with reducing agents such as the aldehyde- or ketone-sulphoxylates. Nevertheless, the production of discharge prints on dyed acetate rayon presents problems in practice that have not been completely solved. In the first place, the resistance of the fibre to penetration by discharging agents makes it necessary to use swelling agents in many cases in order to introduce a sufficient quantity of the discharging agent into the material to discharge dark shades. Secondly, the relatively low water-absorptive capacity of cellulose acetate necessitates the use of shallow roller engravings for machine printing, thus reducing the amount of discharging agent that can be put on the cloth, and also causes the prints to have a tendency to halo during steaming. A third difficulty that is encountered is that of removing the decomposition products of many dyes from the fabric after the discharge has been accomplished. If these substances are permitted to remain in the material they oxidise in time to coloured compounds resembling Paramine Brown, which are almost impossible to remove, and which spoil the appearance of white or pale coloured discharge prints[18]. In view of these factors the production of discharge prints on unsaponified cellulose acetate dyed in dark ground shades is very rarely undertaken. Pale and medium shades can be discharged satisfactorily, while dark shades on mixture fabrics such as acetate–viscose or acetate–cotton are obtained for discharge printing purposes by saponifying the acetate portion and dyeing with direct dyes.

The available range of dischargeable acetate dyes is reasonably satisfactory so far as yellows, oranges, and reds are concerned, though a brighter scarlet could be desired. The principal deficiencies of the range are to be found amongst the blues and violets. No really bright blue–violets or pure blues are obtainable, while the existing dischargeable disperse blue dyes are not of high light fastness, their temperature range properties in dyeing are poor, they do not penetrate well, and they give rise to difficulties in that they tend to accentuate fibre, yarn, and fabric defects[19]. In addition, certain of these dyes do not discharge to a satisfactory white when an alkaline discharge paste is used. Blacks, navies, niggers, and bottle greens are very difficult to discharge satisfactorily when direct-dyed with acetate dyes, but, according to Mellor, a suitable navy for discharge purposes may be obtained by means of S.R.A. Discharge Base VI, diazotised and developed with Navy Developer I (BrC), which can be converted to a good black by shading with S.R.A. Yellow IV (BrC)[20]. A similar procedure may also be employed for the production of brown, wine, and bottle dyeings[21].

The adverse effects of the saponification process upon the weight and strength of acetate rayon

fabrics have caused a good deal of attention to be paid to the development of improved methods for producing discharge prints on these materials. Many different aldehyde- and ketone-sulphoxylates have been examined for use as discharging agents, those preferred at present being the sodium, barium, and neutral zinc formaldehyde-sulphoxylates. Cyanamide-sulphoxylic acid, or as it is better known formamidinesulphinic acid, has also been suggested for this purpose[22], either as the free acid or in the form of its sodium, calcium, or zinc salt. Zinc formaldehyde-sulphoxylate is a very good discharging agent, without the aid of swelling agents, for all but very dark ground shades, and as it has little tendency to flush in steaming is probably the most widely used product at the present time. Oxidising agents have also been proposed as discharging agents, a fairly recent example being the suggested use of sodium chlorite[23]. This substance has been found to be compatible with the usual thickening agents, in contrast to the hypochlorites, and is capable of discharging ground shades dyed with anthraquinonoid dyes, e.g. Cibacet Sapphire Blue G (Ciba), when printed, dried, and steamed for a short time.

In many cases sodium or barium formaldehyde-sulphoxylates alone are incapable of discharging medium or dark acetate-dye ground shades, as is also the case to a much lesser degree with the zinc salt. Many different solvents and swelling agents have been put forward as discharge assistants, as for instance glyceryl acetates, glycol chlorohydrin, and glycerol mono- and di-chlorohydrins. In modern practice zinc, calcium, sodium, ammonium, or barium thiocyanate, thiodiglycol, or diethylene glycol is more usually employed. Very often, too, it is desirable to use a combination of assistants rather than any one alone in order to obtain the best results. It should be noted that fabrics printed with colours containing swelling agents require handling with special care before washing in order to avoid cracking or other mechanical damage.

The usual thickening agents for discharge printing pastes are British Gum, crystal gum, textile gum, or gum tragacanth. British Gum is generally used, but in cases where cracking is feared with delicate fabrics gum tragacanth can be employed in its place.

The inclusion of reduction catalysts such as anthraquinone in discharge printing pastes accelerates the reduction process, but these substances are difficult to remove from the fabric, and give rise to discoloured whites. This latter difficulty is said to be avoided by the use of salicylic acid in place of anthraquinone[24], its presence in the printing pastes being claimed to permit the use of shorter steaming times with a consequent reduction in the tendency of the prints to halo, without having any adverse effect upon the quality of the white discharge.

Coloured discharge prints upon unsaponified cellulose acetate fabrics are usually produced by means of vat dyes, but if these are applied by the recipes customary for printing cellulosic materials very imperfect results are often obtained. The colours have a very strong tendency to halo or flush during steaming, partial saponification of the fibre occurs, very poor discharges are obtained on many medium and dark colour ground shades, and there is a tendency for the prints to have a mottled appearance. The quality of the discharge can be improved by the addition of a swelling agent such as sodium thiocyanate or thiodiglycol, while the tendency for the prints to halo is minimised by reducing the concentration of sodium carbonate and of hygroscopic agents in the printing colours, or by employing alternative alkalis, such as trisodium phosphate, sodium silicate, sodium sulphide, borax, or sodium sulphite[25]. Vat dyes may also be applied to cellulose acetate with the aid of zinc or barium formaldehyde-sulphoxylate, the former being used in the absence of alkalis while the latter is best employed with sodium carbonate and a swelling agent such as sodium thiocyanate[20]. Formamidinesulphinic acid has been suggested as a means of producing coloured discharge prints with vat dyes on acetate rayon, either with or without the addition of mild alkalis, in the presence of swelling agents such as monoacetin and sodium thiocyanate[22], but has not been extensively tried in practice as yet.

Vat dyes in conjunction with zinc formaldehyde-sulphoxylate have been used quite widely for the production of coloured discharges on pale and medium ground shades on acetate rayon. Careful selection of dyes is essential, and in most cases the colour yield is not as high as that obtainable from the normal vat dye recipe. The tendency to halo in steaming is greatly reduced, and the discharging effect of the printing pastes is considerably better than when the latter recipe is employed.

The use of sodium formaldehyde-sulphoxylate with 0·5% sodium carbonate in place of the zinc salt results in better colour yields with certain dyes like Ciba Blue 2B and Ciba Brown G (Ciba), and again the prints are not so prone to flush in steaming as when the full amount of sodium carbonate is used. The colour yield is still not as high, however, as that obtainable in the latter case, while the discharging properties of colours made up by this recipe are much poorer than those containing zinc formaldehyde-sulphoxylate.

The normal vat dye recipe is often used in spite of its limitations upon the thicker acetate fabrics such as locknits, and also upon pale cross-dyed mixture fabrics containing cellulose acetate in conjunction with cellulosic fibres, and gives satisfactory results in these instances.

The esterified leuco derivatives of vat dyes, commercially known as Indigosols (DH) or Soledons (ICI), may be used in conjunction with zinc formaldehyde-sulphoxylate to produce coloured discharge prints on cellulose acetate. Originally the development procedure recommended was to hang the prints in air after steaming and then to regenerate the parent vat dyes by oxidation in an acid bath containing sodium dichromate[26]. Unfortunately this latter treatment often has an adverse effect upon the quality of any white discharge prints present. A later modification of the style employs an addition of sodium nitrite to the

printing colours, development being effected with acidified sodium dichromate as before[27]. Neither process has been employed in practice to any extent so far as is known.

The application of thiocyanate swelling agents to the dyed fabric by padding and drying before printing, rather than by inclusion in the printing pastes, has been proposed[28], and is said to result in better and sharper white discharges, to avoid printing troubles due to the interaction of acidic white discharge pastes with alkaline colour pastes, and to prolong the life of screens in screen printing by removing agents from the printing colours liable to attack the screen fabric. The introduction of a swelling agent into the fibre by padding would also appear to offer the advantage of a more constant concentration of the reagent in the cloth than is easily obtainable in printing, where so many factors influence the amount of printing paste deposited on the fabric.

Another suggested process[29] for the production of discharge prints on acetate rayon that is worthy of mention avoids the difficulty of introducing a sufficient quantity of discharging agent into the fibre, by applying the colours for the ground shade by padding and drying, so as to leave the majority of the colour on the surface of the material. The fabric is printed with suitable discharge printing pastes while in this condition, after which it is steamed for a few minutes to effect discharge, hung in air to destroy any residual reducing agent, and steamed again to complete the fixation of the ground shade. The process might, however, prove somewhat difficult to employ on a large scale.

The drying of discharge prints on acetate rayon requires particular care, as underdrying can lead to a loss of reducing agent prior to steaming, with resultant irregularities in discharge and colour yield, while overdrying is also bad, as it can apparently inhibit discharge without hindering the fixation of vat dyes[30]. Steaming should be carried out as soon as possible after printing so as to avoid exposure marks, while rather drier steaming conditions should be used than are customary for discharge work on viscose materials. In many cases it is desirable to pad the printed goods in a weak solution of sodium *m*-nitrobenzenesulphonate at a printing machine with the twofold object of removing any scum of reducing agent on the surface of the cloth, and of decreasing the tendency of the prints to halo during steaming.

In devising a washing-off process for discharge prints on cellulose acetate materials, it is necessary to take account of the increased difficulty experienced in oxidising vat dyes when applied with the aid of zinc formaldehyde-sulphoxylate, as well as the high resistance to removal from the fabric of many dye decomposition products. Vat discharges on acetate locknit fabrics, or cross-dyed mixture cloths, that have been dyed in pale shades are rinsed well in water, oxidised in dilute sodium percarbonate solution, soaped, and rinsed. Vat colour prints in which zinc formaldehyde-sulphoxylate has been employed, on all-acetate materials, are given a preliminary rinse followed by a more vigorous oxidising treatment in warm ammoniacal sodium perborate solution, after which they are soaped and rinsed. In the case of medium or dark ground shades produced with acetate dyes on unsaponified acetate rayon, the selection of dyes whose decomposition products are relatively easily removed is of the first importance, while a thorough rinsing treatment in cold water before oxidising any vat dyes present assists in the production of satisfactory white discharges. An alkaline washing treatment has been found to assist in the removal of dye reduction compounds[30], the use of baths containing 0·1–1·0% sodium hydroxide being suggested, used under conditions such that no deleterious effect upon the fibre results; while improved white discharges, particularly where these have been adversely affected by oxidation treatments, are said to be obtainable by means of a treatment in an alkaline bath containing a dispersing agent, an oxidising agent, and a finely divided solid adsorbent, suitable ingredients being for example magnesium hydroxide, the sulphuric ester of a higher fatty alcohol, sodium perborate, and a small amount of sodium carbonate[31].

The production of discharge prints on dyed nylon fabrics involves very similar problems to those encountered in the case of acetate rayon, owing to the hydrophobic nature of the two fibres, and similar practical precautions in printing and steaming are necessary. As stated by A. K. Saville[6], no single group of dyes can provide a complete range of satisfactorily dischargeable ground shades for nylon at present, and even when a selection is made from the disperse and water-soluble acetate dyes, the acid class, and the direct dye group, no strong navies, niggers, or blacks of a suitable nature can be found. Yellows, oranges, reds, and scarlets are obtainable with acetate dyes, but the blues and violets are less satisfactory.

Reducing agents such as sodium or zinc formaldehyde-sulphoxylate are suitable discharging agents, and, as distinct from cellulose acetate, swelling agents or other assistants, other than a wetting agent in certain cases, are not required. Zinc formaldehyde-sulphoxylate produces white discharges in a number of instances that darken on exposure to light and air rather more than when the sodium salt is used, and the latter is therefore to be preferred, although it has a greater tendency to flush or halo in steaming.

Coloured discharges are obtainable by means of selected vat dyes printed by the normal vat recipe, but these prints have a very high tendency to flush in steaming, which can be reduced to some extent by a reduction in the amount of glycerol or other hygroscopic agent present and the use of thickenings of a high solid content. It is of interest to note that it has recently been found possible to apply certain vat dyes to nylon in the presence of only 0·1–1·0% sodium carbonate[32], in place of the usual amounts. Discharge printing colours made up in this way are much less liable to haloing troubles during steaming, while the colour yields are very little affected. Unfortunately a number of the vat dyes applicable by this process possess a much lower light fastness on nylon than they do

on cotton, which will prevent their use for a number of purposes.

Washing off after printing is carried out in the same way as with discharge prints on acetate rayon. The oxidation of vat dyes on nylon is much more difficult than is the case when they are applied to cellulosic fabrics, and the use of an oxidation treatment, with sodium perborate and ammonia for instance, is essential.

## CONCLUSION

Up to the present time the printing of acetate rayon and of nylon has been almost entirely carried out with disperse acetate dyes. The relatively low fastness to washing, and in some cases to light also, possessed by the prints has, however, stimulated the development of processes for the application of other types of dyes, and a partial replacement of the disperse acetate dyes for printing these fabrics is to be anticipated in the future, unless new members of this class with improved fastness properties can be introduced, or methods found for increasing the fastness of the existing range. On the other hand, the ease of application of the disperse dyes should ensure their continued use for the numerous purposes for which their fastness properties are adequate, while their suitability for colouring Terylene, Orlon, and other new hydrophobic fibres provides a new and important outlet for this type of colouring matter.

The need to steam prints of disperse acetate dyes on acetate rayon or nylon for long periods in order to obtain optimum colour fixation is a serious disadvantage, from the standpoints of both cost and production. The steaming time may be reduced by means of additions of solvents or swelling agents to the printing pastes, but none of the processes devised so far is ideal, and a further investigation of the conditions affecting the speed of colour fixation would appear to be merited. R. H. Munshi and H. A. Turner have instituted an investigation of the conditions affecting the transfer of dye from thickener to fibre during steaming[33], initially with regard to the transfer of direct dyes to cellulose, and it is probable that if the experimental difficulties could be overcome a similar detailed study of the effect of different thickeners, solvents, swelling agents, and steaming conditions upon the transfer of disperse dyes to suitable films of acetate and nylon would yield results of considerable practical value. A complicating factor in such an investigation would, of course, be the state of dispersion of the dye in the thickener film, which would also repay examination. It would be of interest in this connection to know whether the dye pastes available to-day are of an optimum degree of dispersion, or whether finer dispersions still of a stable nature, not tending to reaggregate on storage, are possible.

The disperse acetate dyes have been shown to diffuse much more slowly into Terylene than they do into acetate rayon[16], and as a result are more difficult to fix in printing, but have a much superior wet fastness when fixed, on Terylene than on the latter fibre, a similar relationship also being observed in the case of Orlon. Three methods of colour fixation have been used so far, all of which have disadvantages of one kind or another. Pressure steaming is restricted to batch processing with the equipment available at present, and is therefore an inconvenient method of processing large amounts of material. It is probable that a continuous pressure steamer could be developed, however, if a demand arose, since a continuous pressure dyeing machine has already been constructed to work at pressures up to 50 lb./sq. in.[34], whose sealing mechanism might be adapted for this purpose. The Thermosol process is of considerable interest, but again is likely to require the installation of new equipment for its satisfactory operation. The use of dye carriers is perhaps the fixation method of most immediate interest, as it can be carried out with existing plant. Dye carriers are thought to function by swelling the fibre, thus permitting the dye to diffuse into it more easily, while in the case of printing their moisture-absorptive properties and solvent action on the dye are also of importance in determining their effectiveness in promoting colour fixation. An ideal carrier should be safe to handle, non-volatile in steam, water-soluble, cheap, and compatible with normal printing thickenings in the concentrations required. It should be effective without causing undue shrinkage of the fabric or having any other deleterious effect upon it, and should be easily removed during washing after steaming. No compound fulfilling all these requirements has yet been found, and a further search is required to find a substance with properties more closely approximating to this specification.

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The author wishes to express his thanks to the Directors of the Calico Printers' Association Ltd. for permission to publish this paper.

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## Discussion

Mr. R. J. HANNAY: What effect would high-pressure steaming have on the set of the fabric?

Dr. SHAW: The effect of pressure steaming upon Terylene or Orlon cloths will depend upon the steaming conditions employed, and upon the severity of the setting process to which the fabrics have previously been subjected. Dimensional changes may be reduced, or eliminated, by the use of a suitable setting procedure. For example, it has been found that a Terylene fabric, set by dry heat at 130°C., shrinks appreciably on steaming for 30 min. at 15 lb./sq. in., while the same cloth heat-set at 200°C. is dimensionally stable when steamed under these conditions.

Mr. C. P. ATKINSON: How can a continuous pressure steamer be developed on similar lines to the continuous pressure dyeing machine referred to?

Dr. SHAW: The continuous dyeing machine [34] consists of a padding mangle and a pressure chamber containing the dyebath. Fabric, padded in an aqueous dye solution, passes into the pressure chamber through sealing rollers capable of retaining a pressure of 50 lb./sq. in. The sealing rollers consist of two steel rollers with a rubber roller pressed against them, leakage round the ends being prevented by a series of cross seals. The machine is capable of treating fabrics up to 62 in. in width, and can run at a speed of 25 yd./min. It would appear to be possible to modify a pressure chamber of this kind so as to make it suitable for use as a continuous pressure steamer.

Mr. ATKINSON: What is required in connection with the installation of new equipment for the satisfactory operation of the Thermosol process?

Dr. SHAW: Existing plant such as high-temperature stenters and dry-heat nylon-setting machines may be used for the Thermosol process. Temperatures of 180–250°C. are required, the treatment times ranging from 5 to 60 sec. The fabric should be heated uniformly, and the temperature maintained as constant as possible throughout the run, in order to avoid irregularities in dye fixation. Cloth tension should be controllable.

Mr. ATKINSON: Will the dye carrier method make it unnecessary to develop plant to operate under pressure, and will it be possible to obtain satisfactory dyed results in heavy shades on present conventional machinery?

Dr. SHAW: It is not yet possible to forecast which of the three methods discussed for the fixation of disperse acetate rayon dyes on Terylene or Orlon will ultimately be preferred. The discovery of a suitable dye carrier of low cost would undoubtedly result in the adoption of this method of fixation, rather than the use of pressure steaming or dry heat, since it would avoid the necessity of purchasing new plant. No such substance is, however, yet known.

Mr. F. CROMPTON: Is 220°C. a steam heat or a dry heat?

Dr. SHAW: The Thermosol process employs dry heating by means of hot air or a heated metal surface to fix disperse acetate rayon dyes on Terylene, etc.

Mr. E. E. BOWKER: The property of sublimation of individual members of the disperse acetate rayon dyes is of vital importance in their application as printing colours. What is their behaviour on Orlon and Terylene in this respect, and would the presence of a solvent or carrier be likely to cause any alteration?

Dr. SHAW: So far as Terylene is concerned, no sublimation has been experienced when using the non-subliming disperse dyes normally recommended for printing. It seems likely that a similar result would be obtained in the case of Orlon also. The use of a dye carrier would be expected to reduce to some extent the tendency of an acetate rayon dye to sublime when printed on Terylene or Orlon.

Mr. H. R. HADFIELD: Is the cuprous ion method of dyeing Dynel (or other polyacrylonitrile fibres) applicable to a printing technique? This method is based on the property of cuprous salts of increasing the exhaustion on Dynel of Solacets (and some acid-type dyes) several times.

Dr. SHAW: It is not possible at present to say with any degree of certainty whether the cuprous ion method of dyeing polyacrylonitrile fibres is adaptable for use in printing. In view of the efficacy of the process, however, such a possibility would appear to be well worth investigation.

Mr. F. V. DAVIS: Can resist styles be produced on acetate rayon and nylon?

Dr. SHAW: No method has yet been evolved for the production of resist prints under disperse acetate ground shades on either acetate rayon or nylon cloths. It has been found possible, however, to devise means of resisting dyes of other classes when applied to these fabrics, as for instance oxidation colours such as Diphenyl Black, or Paramine Brown, on cellulose acetate, or acid dyes on nylon. So far, resist styles on acetate rayon have proved to be very difficult to apply in practice, because of the low absorptive properties of the fibre. Experience with such styles on nylon is much more limited, but here again, in many cases, serious processing difficulties are probable for the same reason.

Mr. H. A. BRASSARD: Has any work been done on ultrasonic printing?

Dr. SHAW: So far as is known, no ultrasonic process for the fixation of prints has yet been developed.

Mr. C. W. SEELEY: When using certain acetate rayon dyes for printing, particularly of the Dispersol Fast Red RS type, along with natural gums or prepared textile gums as thickeners, loss in colour value has been experienced when the made-up printing paste has been kept 5–15 hr., while pale shades are almost destroyed. Has the author had a similar experience?

Dr. SHAW: I have not encountered the loss in colour yield described. Since the loss of dye appears to be associated with the gum used for thickening the printing paste, the possibility of using an emulsion thickener such as that described by Krause and Wainwright[5] might be considered.

Mr. R. L. HILL: Is the use of mechanical emulsifying equipment, such as the Q.P. Homogeniser, recommended for the improvement of the printing properties and colour yield of the disperse type of acetate rayon dyes in printing?

Dr. SHAW: Print pastes prepared from acetate dyes in paste form are not usually improved in colour yield by homogenisation. A treatment of this kind is, however, useful to correct a faulty print paste in which the dye is so poorly dispersed as to give rise to "specky" prints.

Mr. E. STEAD: Would something like the Standfast molten metal dyeing machine be likely to succeed where high-temperature fixation processes are required?

Dr. SHAW: The use of molten metal as a heating medium for the fixation of dyes by the Thermosol process offers the advantages of rapid heat transfer and uniform heating. It is, however, doubtful if the method would be applicable in practice, since when using temperatures of 180–250°C. it would not be possible to retain the aqueous baths on top of the metal that are a feature of the Standfast process. In the absence of these aqueous layers covering the metal, the rapid formation of oxide scum and the carry-over of metal alloy by the fabric are to be expected. Furthermore, the heating time required for the operation of the Thermosol process is normally considerably longer than the dyeing times employed in the Standfast process, which would necessitate either the use of a larger metal bath, with a consequent increase in cost of installation, or the use of running speeds as low as 3–4 yd./min. in extreme cases.

Mr. C. P. TATTERSFIELD: Has the Thermosol process any application for fixing disperse acetate dyes on acetate rayon, thereby saving considerable time compared with the normal steaming process?

Dr. SHAW: Disperse acetate dyes can be applied to acetate rayon by the Thermosol process. It is very doubtful, however, if the method is of practical value in this instance, since the heating conditions required are approximately the same as for the fixation of the same dyes on Terylene, and are likely to cause damage to the fibre.

Mr. H. A. TURNER: Mr. Daruwalla, working in our Department, has already made some progress in a study of the migration of acetate rayon dyes from thickener to fibre, by steaming together films of thickener containing acetate dyes with sheet cellulose acetate and sheet 66 nylon. With the former we have used a small selection of disperse (Duranol) dyes and their corresponding soluble (Solacet) forms. In no other dye class which we have examined by these methods have we found so close a correspondence between dyeing and printing behaviour. We have used pure insoluble dyes ground in water to various stages of subdivision. We find evidence of a very high equilibrium exhaustion, which appears to be independent both of the initial concentration of dye in the thickener phase and of the fineness of dispersion, although, naturally enough, the time in which equilibrium is attained increases with increasing proportion of dye in the system and with increasing coarseness. The exhaustion of the pure Solacet form is low, and although it increases with added salt, its final exhaustion falls far short of that of the dispersed form. There have been some interesting results which indicate that the dispersion of the dye in the thickener film takes place on steaming before much transfer to the acetate occurs.

SATURDAY MORNING, 22nd SEPTEMBER 1951

*Chairman*—Mr. H. H. Bowen

# The Yarn Producer's Problems in the Dyeing of Nylon

H. J. Palmer

The factors in the molecular structure of 66 nylon which control its dyeing properties are identified. Amine end-group content and degree of order are shown experimentally to be the most important. Examples are given of the use of the experimental work in (*a*) the control and investigation of the nylon production process, and (*b*) the choice of dyes of good levelling and covering properties on nylon. On the basis of the latter a classification of anionic dyes is proposed.

## 1—Introduction

The progress of knowledge of the fundamental processes involved in the dyeing of the early man-made fibres was slow. The practical dyer had to limp along using his empirical knowledge gained by experience with related, but different, natural fibres. Systematic work in the laboratory had to be done before the dyeing of the viscose and acetate rayons was put on a logical basis. With every synthetic fibre the yarn producer, the dyer, and the dyemaker have always to combine to investigate and overcome the dyeing problems associated with the fibre. The history of nylon is unique in that the research worker has been able, on the whole, to keep abreast of the problems encountered by the commercial dyer. In fact, the laboratory worker is now in some ways ahead of the dyer. It does not seem too much to hope that, when new fibres are developed in the future, the investigation of fundamental dyeing characteristics will precede the commercial exploitation of the fibre. The development of Terylene seems to be following this pattern[1].

Every dyeing may be considered to involve two main factors—the yarn or fibre and the application of the dye. If one is poor, the quality of the finished material suffers. The yarn quality is largely governed by the yarn producer. The quality of the dyeing depends on the skill and knowledge of the dyer together with the characteristics of the dyes supplied by the dyemaker. Only the rôles of the yarn producer and the dyer need concern us here. The dyer relies on the yarn producer to provide good-quality yarn. The producer expects the dyer to produce a finished dyeing worthy of the original yarn. Obviously, then, some compromise and co-operation between the two points of view are vital for the production of a good dyed product.

This paper is concerned primarily with the contribution of the yarn producer to the solution of some problems in the dyeing of continuous-filament 66 nylon. Any success the work has had is at least partly due to the friendly co-operation between the interests involved. Detailed results will be given only where they amplify a point of view. A brief résumé of some facts about the dyeing of nylon is useful here.

## 2—The General Position of Nylon Dyeing

The dyeing of nylon is in some ways easy, in others difficult. Whilst the techniques used for the natural fibres cannot be used without modification for nylon, it is possible to apply dyes by adaptations of older methods. Fortunately, no attempt has been necessary on the part of dyemakers to produce a special class of dyes. Enough dyes are available to give a range of shades of reasonably good fastness. The difficulties met in the dyeing of nylon have undoubtedly been lessened by the experience gained in the dyeing of the older man-made yarns. Problems, of course, have arisen, but largely because nylon is different from any other fibre, either natural or synthetic. No one expects to be able to dye cotton in the same way as wool. Similarly, established concepts must be modified when the dyeing of nylon is considered.

### 2.1 The Dyer's Problems

Both soluble anionic and insoluble disperse dyes may be applied conveniently to nylon. Most other classes of dyes can be applied, too, but either application difficulties or the durability of the finished dyeing make their widespread use inconvenient, as yet.

The first difficulties noted by the commercial dyer about the application of dyes to nylon included—

1. Often a fairly high dyebath temperature has to be used.
2. Dyes which had come to be regarded as "levelling" do not level well on nylon.
3. Deep shades are difficult to obtain.
4. Many mixtures of anionic dyes which have been found to be compatible on other fibres are not compatible on nylon.

The first two of the above difficulties are largely governed by the inherent fine structure of the yarn. The closely knit molecular structure of nylon, which imparts the high tenacity, also hinders the ingress of both water and dyes. The low moisture regain of nylon is partly governed by this closely packed structure.

The last named pair of problems were shown to be caused primarily by the small number of dyeing sites available in the yarn[2]. Insufficient anionic dye can be taken up by nylon to produce heavy shades. In a mixture of dyes, one component may have a much higher diffusion rate than the others, and this dye may enter the yarn so rapidly that all the dyeing sites are occupied before any of the other components can enter. Mixtures of dyes with different diffusion rates are incompatible. Compatible mixtures are those in which the components have similar diffusion rates in admixture.

These problems were solved or lessened by the dyemakers. By either empirical tests or measurements of rates of dyeing and diffusion, suitable dyes and dye mixtures were chosen to produce level shades, of medium depth, at reasonable dyeing temperatures.

Whilst the position was reasonably satisfactory for the current uses of nylon yarns, there were still several undesirable features of nylon dyeing from both the theoretical and the dyehouse points of view. The practical difficulties caused by the small number of dyeing sites (amine end-groups) are still present. Not only could the problems which have already been mentioned be lessened, but also other day-to-day difficulties could be alleviated by an increase in the number of dyeing sites in the yarn. Trials are now continuing which indicate that it is possible to produce nylon yarn of increased amine end-group content, which is comparable in dyeing properties to natural silk.

Now the difficulties introduced by the closely knit fine molecular structure of nylon yarn are less easy to overcome. Dyebath assistants do help, of course, in the production of level dyeings; colourless sulphonated bodies are particularly helpful. Reduction in the temperature necessary for dyeing is less easy, and various attempts have been made to open up the structure of the yarn by means of swelling agents. The swelling treatment may be applied either before or during dyeing. Generally, no worthwhile increase in the rate of uptake of the usual dyes is obtained. However, since there are so many potential swelling agents which might be of value, further work on this approach may be rewarding.

### 2.2 THE YARN PRODUCER'S PROBLEMS

One aspect remains as a problem in the dyeing of nylon, namely yarn irregularities. Every natural and synthetic textile material exhibits some dyeing irregularity. The amount of variation which can be accommodated in continuous-filament yarns is much lower than in staple fibres. In the older regenerated yarns, gross erratic variations have been removed by process control measures. There still remain, however, irregularities which are inherent in the method of production of the yarn. The variation between the inside and the outside of a viscose cake is an example of this type of irregularity. Natural fibres also have these inherent irregularities; the "root-to-tip" variation shown by wool is an example. The inherent variations govern the use to which the yarn may be put; the yarn is satisfactory only if the faults do not show in the final fabric. The problem with nylon was to detect those yarn properties which controlled the dyeing characteristics. A study of such properties showed how far it was possible to eliminate irregularities, and to what extent the irregularities were inherent in the yarn-manufacturing process. The best way of covering the inherent dyeing irregularities was then investigated. This paper is intended to sketch the mode of approach to the problem and the ideas and intentions arising from the results of the investigation. Final results are, of course, difficult to give, especially as the investigation is still continuing and nylon production and dyeing techniques are steadily improving.

Only differences in the dyeing properties of continuous-filament 66 nylon yarns caused by differences in the chemical and physical structure of the yarn will be considered. Other differences, such as filament denier, will not be considered.

## 3—Investigation of the Sources of Dyeing Irregularity

### 3.1 SOURCES OF VARIATION

Variation in the dyeing properties of a continuous-filament nylon yarn may be of either short period or long period (within-package or package-to-package variation). So-called dyeing differences in a dyed fabric may arise from two causes, namely differences in the amount of dye absorbed and differences in the light-reflecting properties of the undyed yarns. Two yarns of the same denier containing exactly the same amount of dye may apparently differ completely in depth of dyeing simply because they differ in light-reflecting properties. The influence of twist on the appearance of a dyed fabric is a well known example of this type of phenomenon. A surprisingly small amount of information is available in the literature about the factors in the molecular structure of a textile yarn which may be expected to govern the amount of dye taken up by the yarn. For example, it was not certain how far the fine physical structure of nylon governed the amount of dye taken up at equilibrium. Sufficient deductions could be made, however, to start an investigation of the important factors.

In commercial dyeing it is not usual to saturate the material completely with dye, so that we are mainly concerned with the rate of uptake of the dye by the yarn. This rate is dependent on two factors (assuming that factors such as filament denier, etc. are constant)—

1. The equilibrium dye uptake of the yarn. The greater the uptake the faster the rate.

2. The fine physical structure of the yarn. The more closely knit the molecular structure the slower the rate.

Peters[2] has shown that the major factor which influences the equilibrium absorption of anionic dyes by nylon is the amine end-group content. This is, therefore, a yarn property which has to be investigated as a source of dyeing variation, especially since, as dyeing proceeds, equilibrium is more nearly reached, and so variation in amine end-group content becomes the major cause of dyeing variation.

The variation in the fine structure of the yarn may be divided, as a first approximation, into two main types. Firstly, the overall degree of order or crystallinity may vary. Nylon is "melt-spun", and differences in the cooling conditions can give differences in degree of order. Then, the degree of molecular orientation may also alter. As is well known, nylon yarn is cold-drawn during manufacture to produce a high degree of longitudinal molecular orientation[3]. Some types of tension

differences during processing also influence orientation. Variations, therefore, are to be expected in the amount of molecular orientation. Dyeing differences in viscose rayon are often attributable to differences in the degree of orientation [4].

To investigate the influence of these molecular properties on dyeing characteristics, yarns were produced containing known chemical and fine structure differences. The properties were characterised as far as possible by independent methods. Amine end-group content was estimated by conductimetric titration of the solution of nylon in phenol–methanol solvent with hydrochloric acid in methanol. Carboxyl end-groups were estimated by titration in benzyl alcohol solution with potassium hydroxide in methanol.

The characterisation of the fine structure of the yarns is less easy. X-Ray analysis and birefringence and density determinations are too insensitive to detect differences of the magnitude with which we are concerned. Measurement of the changes in length of the yarn in aqueous phenol solution and estimation of the phenol partition coefficient were used [5].

In the practical work all samples were scoured in a 1% (vol./vol.) Dispersol VL (ICI) bath, at 70°C. for 30 min., before dyeing. A liquor ratio of 50 : 1 was always used in the dyeings. The fabrics were set in steam at 25 lb./sq. in. for 2·5 min. The concentration of dyebath constituent is expressed, in the usual way, as a percentage of the weight of nylon dyed.

### 3.2 DIFFERENCES IN FINE PHYSICAL STRUCTURE

An earlier paper [5] has described how orientation was chosen for the initial investigation, since variations in the dyeing properties of other synthetic yarns are known to be caused by orientation differences. It was quickly found that orientation differences are not a serious source of dyeing variations in nylon yarns. Provided any associated denier variation cannot be detected visually, the influence of orientation variations on the dyeing rate of the majority of disperse and anionic dyes is unimportant. In contrast, differences in degree of order are very serious; however, they may be considered together with the orientation differences, since their mode of action is similar to that of the latter. Changes in both factors produce dyeing differences only by slowing down the rate of entry of the dye; the amount taken up at equilibrium is relatively uninfluenced by differences in fine structure.

One pair of isotherms (Fig. 1) serves to illustrate all the results obtained in the work on the influence of differences in the fine structure of nylon on its dyeing properties. Let us consider two yarns of the same chemical composition, but differing in fine structure. These yarns are then dyed with either an anionic or a disperse dye. Both yarns eventually contain the same amount of dye (*C*, Fig. 1). When the yarns differ only in orientation, after a normal dyeing time, say 1 hr., point *C* is usually reached with most anionic and disperse dyes. With some orientation-sensitive dyes, only point *A* is reached after 1 hr., and there is a difference between the depths of dyeing of the yarns. If dyeing is continued, the difference between the appearance of the dyed yarns becomes less, e.g. at point *B*, until finally the two yarns are of the same depth of shade (*C*).

The behaviour of yarns of different degrees of order is similar to that of yarns differing in degree of molecular orientation; only the time scale of Fig. 1 is altered. With disperse dyes, point *C* is usually reached after a normal dyeing time, say 1 hr. The dyeing rates of anionic dyes are more sensitive to differences in degree of order. After 1 hr. dyeing with an anionic dye, only point *A* is reached, and so the yarns differ in depth of dyeing. The difference becomes less as dyeing proceeds, and finally point *C* is reached after several hours' dyeing. This time is longer than any that the commercial dyer may use, and so these degree-of-order differences are very serious. In fact, from the viewpoint of the commercial dyer, who uses only relatively short dyeing times, the dyeing differences caused by variations in degree of order may be considered to be differences in the amount of dye it is possible for the fibre to take up.

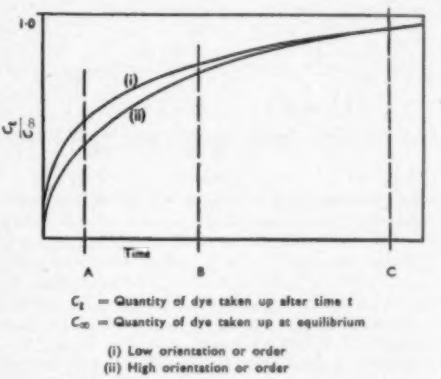


FIG. 1—Schematic Representation of the Course of Dyeing of Yarns differing in Fine Physical Structure

An attempt was made to relate the topographical characteristics of the dye molecules to the influence of the fine structure of the nylon on their dyeing rates. Little success was achieved. On the whole, those dyes which have large irregularly shaped molecules and temperature-sensitive dyeing rates are particularly sensitive to differences in fine structure. Degree of sulphonation and position of sulphonic acid groups also seem to play a part.

### 3.3 DIFFERENCES IN AMINE END-GROUP CONTENT

The relative importance of variations in fine physical structure was established by the preceding work (§ 3.2). The importance of amine end-group contents has already been mentioned (§ 3.1), and has been further underlined by the present investigation. Both the dyeing rate and the equilibrium uptake of all anionic dyes tested are dependent on amine end-group content. The

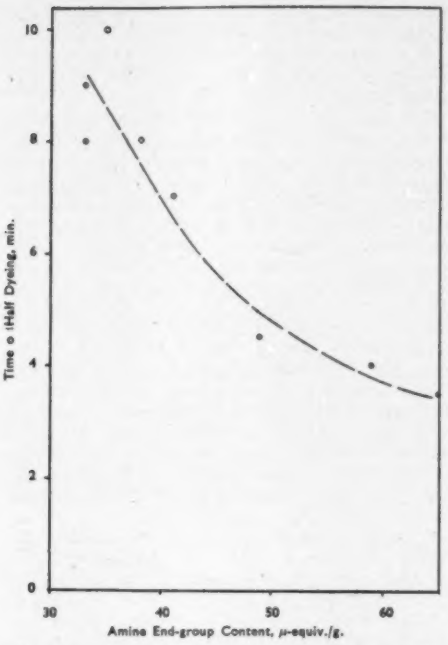


FIG. 2—Relationship between Amine End-group Content and Time of Half Dyeing in a Solway Blue B Dyebath

dyeing rate method previously described [5] was used to find the dependence of the dyeing rate of Solway Blue B (ICI) on amine end-group content. A dyebath was used at 90°c. which contained 2% dye and 2·5% acetic acid. Fig. 2 shows that the rate of dyeing, which is inversely proportional to the time of half dyeing, is increased by increase in amine end-group content.

Peters [2] showed that the uptake of only certain anionic dyes exhibited a stoichiometric relationship to amine end-group content (e.g. Solway Blue B [5], Naphthalene Scarlet 4R—Fig. 3). With others, more dye was taken up than corresponded to the basic groups of the nylon. A number of dyes were shown by the present work to exhibit this behaviour, notably the "neutral-dyeing" wool dyes and soluble dyes for acetate rayon (e.g. Solacet Fast Scarlet B—Fig. 3). These results were obtained using 10% dyebaths containing 2·5% acetic acid at 90°c. for 5 days. Now these same dyes, when applied to nylon, do not show up amine end-group variations as much as those which exhibit a stoichiometric relationship, because the percentage change in dye content for a given change in amine end-group content is lower. These dyes, then, may be used to cover usual chemical variations.

Amine end-group content, or an associated fine structure difference, influences the amount of disperse dye taken up by a nylon yarn. The influence is very slight; wide variations produce differences in disperse dye uptake of the order of only 5%, and since experimental error is high with disperse dyes, the unambiguous detection of such small differences is very difficult. However, these differences are of importance to the commercial dyer.

Some work was done on the dependence of the dyeing properties of vat and basic dyes on amine end-group content, mainly to investigate their suitability for yarn characterisation tests. The uptake of basic dyes is a function of pH and the relative amounts of amine and carboxyl end-groups. The uptake of vat dyes in either the leuco or insoluble form is uninfluenced by amine end-group content. The rate of dyeing, however, is dependent on fine structure in much the same way as orientation-sensitive anionic dyes.

### 3.4 DIFFERENCES IN LIGHT-REFLECTING PROPERTIES

The influence of the inherent light-reflecting properties of the substrate on the appearance of a dyed fabric has already been mentioned (§ 3.1). The investigation of the fundamental light-reflecting properties of the filaments of nylon is very difficult. The simplest approach seems to be the construction of polar diagrams for pads of nylon, wound in contiguous turns. From these diagrams it is possible to identify roughly the light reflected from inside the filaments and that from their surface. Generally speaking, it appears that it is variation in the light-reflecting properties of the inside of the filaments which produces the usual variations exhibited by nylon yarns. By their very nature these differences are not covered any more efficiently by dyes exhibiting particular dyeing characteristics. The best procedure is to apply dyes of colours, namely yellow and orange, which do not accentuate fabric faults.

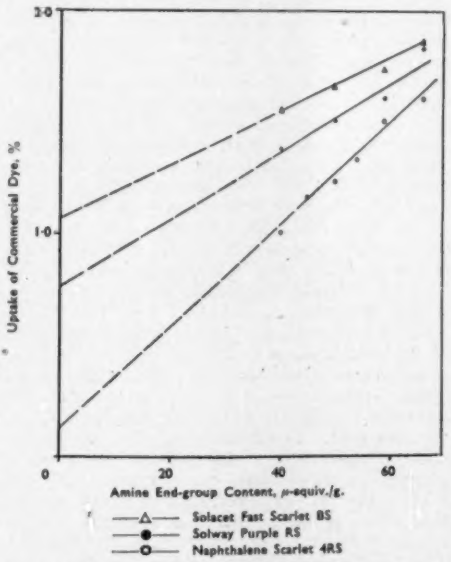


FIG. 3—Relationship between Dye Uptake and Amine End-group Content for Various Commercial Dyes

## 4—Investigation and Control of Dyeing Variations in Nylon Production

### 4.1 ROUTINE DYEING TESTS

Now, on the basis of the foregoing experimental work, two types of investigations may be made. Firstly, quality control and plant investigation tests can be done to identify the occurrence of differences in physical and chemical structure in nylon yarn which give rise to dyeing differences. Secondly, the results may be used to help the commercial dyer to produce even dyeings. Many hundreds of results are required to obtain either a true picture of the magnitude and nature of the differences present in the yarn production or to assess the relative merits of dyes. Some rapid method of testing is, therefore, obviously necessary. Two types of test were developed—

(*a*) In the "dye depth" test, a circular knit tube, or preferably a weft satin ribbon, is prepared containing 6-in. sections of fabric from each bobbin under test and a number of control sections from a standard bobbin of known characteristics. After setting, this fabric is dyed under standard conditions, and differences in the depth of dyeing between the sample panels and the control are estimated by means of a photometer. This photometer is a null-point instrument developed by us, which incorporates vacuum photocells and a D.C. amplifier, supplied by the Baldwin Instrument Co. It is a stable instrument and is used by unskilled personnel to provide hundreds of readings in a day.

(*b*) In the other type of test, a sample of yarn in hank form is dyed to equilibrium in a small dyebath. The amount of dye remaining in the dyebath is estimated colorimetrically, and then from the original concentration of the dyebath the concentration of dye in the yarn may be calculated. This test is known as a dye uptake test.

In the investigation of the dyeing properties of nylon yarn production, dyes and dyebath conditions for use in these two tests were chosen to accentuate a particular type of difference in yarn structure. One dye, Naphthalene Scarlet 4R, was chosen because, under the dyebath conditions used, its dye uptake is proportional to amine end-group content and is uninfluenced by the usual differences in degree of order and orientation. Solway Blue B was used because the depth of dyeing obtained is sensitive both to amine end-group content and to the usual differences in degree of order, but is not influenced by orientation differences. Differences both in degree of order and in orientation were detected with Caledon Dark Blue B, which is not very sensitive to amine end-group changes. Indoine Blue B may also be used for accentuating differences in fine structure. It is a basic dye having a large molecule and it is relatively insensitive to chemical differences of the order usually encountered. Summarising, then—

(*a*) Differences in amine end-group content are detected by means of the dye uptake test using—

| | | |
|---|---|---|
| 2% | ... | Naphthalene Scarlet 4RS (*C.I.* 857) |
| 2·5% | ... | Acetic acid |

for 5 hr. at 90°C.

(*b*) Differences in degree of order are detected by means of the dye depth test, using—

| | | |
|---|---|---|
| 2% | ... | Solway Blue BNS (*C.I.* 1054) |
| 2·5% | ... | Acetic acid |

for 1 hr. at 90°C., in conjunction with the preceding test (*a*).

(*c*) The dye depth test using either Caledon Dark Blue B or Indoine Blue B may be employed to detect differences in fine structure. In conjunction with test (*b*) using Solway Blue B differences in orientation may be identified—

| | | |
|---|---|---|
| 2% | ... | Leuco Caledon Dark Blue B (*C.I.*1099) or Indoine Blue B (*C.I.* 135) |
| 0·1% | ... | Dispersol VL (ICI) |

for 1 hr. at 90°C.

(*d*) The inherent light-reflecting properties of the yarn may be characterised, by photoelectric means, using either the scoured, set fabrics before dyeing, or preferably by measurements on pads.

### 4.2 PLANNING AND INTERPRETATION OF DYEING INVESTIGATIONS

The application of the foregoing tests is not straightforward, for the following reasons—

(i) No test is a unique function of a particular type of difference in yarn structure. For example, whilst the dye uptake test using Naphthalene Scarlet 4R is not sensitive to usual differences in degree of order, some types of such differences may influence the value obtained.

(ii) A given yarn property is dependent on many factors in the nylon production process.

(iii) The division of fine structure into two is an oversimplification. Degree of order can vary in many ways; for instance, two samples may possess the same overall degree of order, but the average size of ordered regions may be different.

(iv) A given sample of yarn usually differs in more than one characteristic from its fellows. This behaviour is particularly pronounced in nylon[5].

(v) Most dyeing tests are comparative and not absolute, especially when carried out by unskilled personnel. Even the skilled dyer matches the shades required, by addition of further dye.

The foregoing difficulties can be solved only by the use of statistical methods. The particular characteristic it is desired to investigate or control must be decided upon, and then the sampling and testing scheme chosen. The rewards of careful planning and interpretation of dyeing investigations of the type to be described are so great that a brief description of the mode of approach adopted is fitting.

In any trial, the method of sampling and size of sample must first be decided. Usually, intelligent guesses can be made as to the likely sources of variation in the process, so that a sample size can be decided upon which is manageable and which takes account of the likely sources of variation. One point of interest in this connection is that, when only sample-to-sample variation is being investigated, it is better to take single

samples from a large number of specimens than to take duplicate samples from half the number of specimens.

Bias in both sampling and testing must be guarded against. When day-to-day variation is being assessed, it may be misleading, for example, to ignore the time of day at which samples are taken. A good example of bias in testing is the way in which replicate dyebaths may differ, so that if each day's samples are dyed separately, an apparent day-to-day difference may be introduced. Only intelligent use of control bobbins can overcome this type of difference. Another example actually encountered during the present work was introduced by the circular knitting machine used to prepare the knitted tubes for the dye depth tests. On occasions the stitch size of the fabric given by the machine was found to alter with time. On knitting samples systematically, this variation in stitch size could not be separated from variations introduced by more important factors. Photometer measurements on the set undyed panels are dependent on stitch size, and they show this bias (Fig. 4). Adequate randomisation of samples and the careful use of control bobbins are the only ways of eliminating bias in both testing and sampling.

An efficient analysis of the results is just as important as the planning of the experiment. The considerations used as the basis of the sampling plan may often be used to indicate the preliminary type of analysis required. Graphical presentation of the results, as they are obtained, may be used for the preliminary analysis. This presentation may indicate useful modifications of the original sampling plan, which may be put into operation as the experiment proceeds. Afterwards, a more detailed analysis can be made. From these analyses, it is generally possible to decide on the most important sources of variation and to choose a method of presentation of the results for future use in process control and investigation. Control charts and to a lesser extent correlation diagrams appear to be the most useful way of presenting the results.

An example of the former is given in Fig. 5, which represents the results of a dye uptake test using Naphthalene Scarlet 4RS for a given set of nylon-spinning machines on successive days during an experimental trial. The presence of consistent inherent differences is evident; the means for the X machines are always above those for the O machines. Random day-to-day differences are also evident. At point *A*, a deliberate difference was made to the process as a whole, and all the machines have altered together. At point *B*, individual machines have been made to give low results, so that the range is outside the control limits and the mean of all the results is lowered. The consistent difference between O and X machines has been purposely widened at *C*.

A good example of a correlation diagram is that given in Fig. 6 for dye depth results using Solway Blue B and dye uptake values using Naphthalene

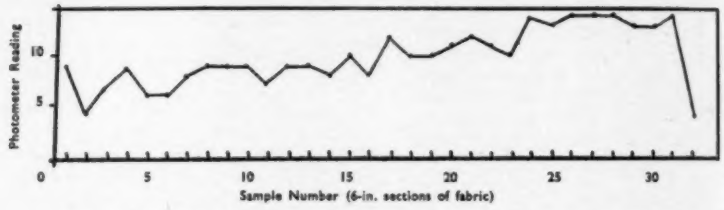


FIG. 4— Graph to illustrate the Change in Stitch Size with Time of Knitting on a Circular Knitting Machine

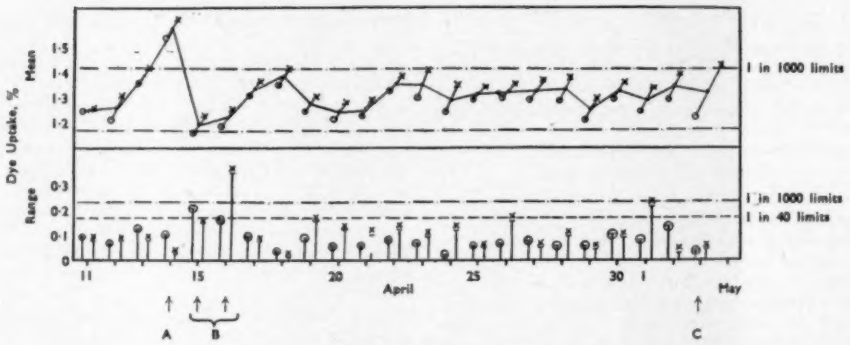


FIG. 5— Control Chart to illustrate Day-to-day Variations in Dye Uptake

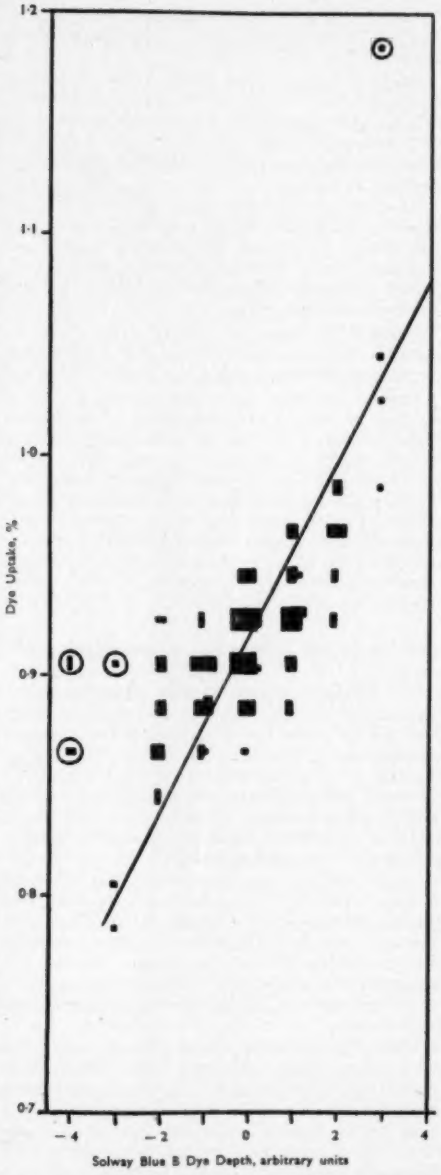


FIG. 6—Correlation Diagram for Solway Blue B Dye Depth and Naphthalene Scarlet 4R Dye Uptake

Scarlet 4R. Whilst the general agreement between the results of the two tests is good, individual samples (ringed in the diagram) of normal or high dye uptake exhibit low Solway Blue B dye depths. These differences were shown by independent tests to be caused by differences in degree of order.

Briefly summarising, in any experiment concerned with the control or investigation of the nylon production process, it is necessary to decide on—

(*a*) The method of sampling, so that all probable variables are covered and bias is guarded against.

(*b*) The method of test to give a true picture of the important variables.

(*c*) The preliminary method of analysing the results, which may modify the approach as testing proceeds.

(*d*) The final method of analysis and presentation of results to gain the maximum information.

It is hoped that these examples will illustrate the mode of approach in the application of dyeing tests to the control and investigation of the nylon production process. These tests are the basis of the "merge number" familiar to every user of nylon yarn.

## 5—Choice of Dyes of Good Covering and Levelling Properties on Nylon

This experimental work is of value to the dyer and, incidentally, to the dye manufacturer, too. Both are interested in dyes of good levelling and covering properties on nylon. It has already been mentioned that measurements of dyeing and diffusion rates are the best means of assessing the covering properties of dyes. However, the methods are time-consuming, and so two arbitrary dye depth tests (§ 4) were developed.

For the assessment of the sensitivity of the dyes to differences in amine end-group content, a weft satin was prepared containing portions of weft from yarns possessing widely divergent amine end-group contents. Portions of the set fabric were then dyed in dyebaths containing sufficient dye for there to be at least half the original concentration of dye remaining after one hour's dyeing. Usually a 5% dyebath, containing 0·5% acetic acid, was used. The differences in depth of dyeing were then estimated photoelectrically. Table I shows that the results of this dye depth test agree well with those for actual dye uptake estimations. The differences are inversely proportional to the covering properties of the dyes with yarns differing in amine end-group content. Therefore, this test can be used to assess the covering properties of dyes.

The routine examination of the dependence of dyeing rates on fine structure is less easy. A comparative dye depth test was developed, in which yarns differing only in fine structure— molecular orientation and degree of order— were dyed together under dyebath conditions chosen to accentuate the differences in the rate of dyeing introduced by the fine structure differences. These dyebath conditions, quite simply, are opposite to those used by the commercial dyer to obtain level dyeings. In other words, a high initial dyeing temperature, low dye concentration, low pH, and short dyeing time were all used. The dyebath conditions were usually 0·5% dye, 5% acetic acid, and 15 min. dyeing at 90°C. The differences in dye depth between the dyed samples were estimated with the photometer. There was a difference

between the values of the phenol partition coefficient of 1·5 units [5] for the two yarns in these experiments which differed in degree of order. The yarn of high molecular orientation had a birefringence of 0·061, whilst the birefringence of the low-orientation sample was 0·059.

Most of the dyes exhibit only slight dependence on molecular orientation (Table I). Some of the dyes are sensitive to orientation, and it has been found that these same dyes level badly on nylon. The results of this test agree well with those of dyeing rate measurements.

Degree of order influences the dye depth of all the anionic dyes tested; disperse dyes are insensitive (Table I). The latter may, therefore, be used to cover both differences in amine end-group content and in degree of order.

These simple tests, based on the more complicated and time-consuming experimental work, may be used to segregate, in a reasonably objective manner, dyes which possess good levelling and covering properties on nylon. From limited small dyehouse trials it appears that dyes which show less than 10% differences in dye depth in each of these tests are suitable for covering usual dyeing differences. It may be noted that only results on blue, red, and green dyes are reported. Usual dyeing differences in yellows and oranges can be covered with most wool-type or soluble acetate rayon anionic dyes.

## 6—Elimination and Covering of Differences in Dyeing Properties

On the basis of results obtained in investigations of the foregoing type (§ 4), it has been possible to find the factors in the nylon production process which cause dyeing differences. Some of these variations can and are being eliminated. Others are inherent in the process. On the basis of present knowledge, it is possible to cover the inherent variations with selected dyes (§ 5). This knowledge may be summarised as follows—

(i) Differences in light-reflecting properties are equally prominent with all types of dyes. Only by the use of pale shades in the spectrum range in which visual response is low (yellow and orange) can the differences be covered.

(ii) Differences in amine end-group content and degree of order are shown up by anionic dyes. Some selected soluble dyes do cover better than the majority; soluble acetate rayon dyes are particularly good. All disperse dyes are satisfactory for covering both chemical and degree-of-order differences.

(iii) Differences in degree of molecular orientation can be covered by the majority of anionic and by all disperse dyes, provided only that any associated denier difference cannot be detected visually. The dyes which do not cover orientation differences can be found by simple tests, and a double advantage is gained by their rejection, since they possess poor levelling properties on nylon. Vat dyes do not cover differences in molecular orientation.

The adoption of a classification of anionic dyes for nylon is convenient. The labels "direct", "neutral-dyeing", "wool dyes", etc. may all be ignored. Such a classification might be made as follows—

Class A—Dyes which cover amine end-group content, degree of order, and orientation differences in nylon, the equilibrium absorptions of which are not stoichiometrically equivalent to the amine end-group content, e.g. Solacet Fast Blue 2B, Anthraquinone Violet.

Class B—Dyes whose rates of dyeing are not sensitive to differences in molecular orientation, but whose absorptions are a direct function of amine end-group content, so that they do not cover amine end-group differences, e.g. Kiton Red 6B, Naphthalene Scarlet 4R.

Class C—Orientation-sensitive dyes, which accentuate orientation differences and possess poor levelling properties on nylon, e.g. Durazol Blue 2R.

Results similar to those given in Table I could be used to make this classification. The advantages of such a system to both dyers and dye manufacturers would be very great. The uses of nylon will undoubtedly develop greatly, so that the establishment of an adequate dye classification now will solve many future problems. The system at present proposed is, of course, only a skeleton; modifications based on fastness properties would have to be made. Conditions are, however, opportune for a start to be made.

## 7—Problems Remaining in the Dyeing of Nylon

The solution of most evident problems in the commercial application of dyes to nylon is in sight. The problems caused by lack of dimensional stability are well under control [6]. Those raised by the use of nylon blended with other fibres can generally be solved by means of empirical tests [7,8]. Fastness requirements for some potential uses of 66 nylon may be difficult to meet; suitable isolated dyes may be found empirically.

There are more gaps, however, in the theory of dyeing. Most of these problems are aspects of the general theory of the dyeing of all fibres. In particular, the influence of fine structure on dyeing rate cannot be explained in terms such as the molecular size of the dye. Possibly factors such as the free energy changes during dyeing should be considered.

Then, the dye–fibre combination for any class of dyes is not fully understood. The rôle of amine end-group content in dyeing with anionic dyes is certainly important, but other factors also play a large part. For example, the lack of stoichiometric relationship between equilibrium dye uptake and amine end-group content is disturbing (Fig. 3). Further, for a given dye, the graph of amine end-group content and dye uptake is not always the same for 66 nylons produced in different ways. The curves are displaced along the uptake axis, so that there is a variable intercept on the uptake axis which is characteristic of the yarn.

The combination of disperse dyes with nylon is also imperfectly understood. The dependence of uptake on amine end-group content was proved by

TABLE I

**Sensitivity of Dyes to Differences in Fine Physical Structure and in Amine End-group Content of Nylon**

| | Dye | *C.I.* No. | 25% $NH_2$ End-group Difference | | Dye Depth Difference (%) caused by— | |
|---|---|---|---|---|---|---|
| | | | Dye Depth Difference (%) | Dye Uptake Difference (%) | Difference in Orientation | Difference in Degree of Order |
| (1) | Carbolan Green G (ICI) ... ... | — | 8 | 10 | 5 | 5 |
| (2) | Solway Green G (ICI) ... ... ... | — | 9 | 10 | 3 | 11 |
| (3) | Carbolan Brilliant Green 3G (ICI) ... | — | 6 | 7 | 15 | 14 |
| (4) | Naphthalene Dark Green A (ICI) ... | — | 14 | 12 | 0 | 8 |
| (5) | Solacet Fast Green 2G (ICI) ... ... | — | 5 | 5 | 0 | 10 |
| (6) | Naphthalene Scarlet 4R (ICI) ... | 857 | 18 | 20 | 0 | 9 |
| (7) | Lissamine Fast Red 3G (ICI) ... ... | — | 18 | 20 | 13 | 6 |
| (8) | Solacet Fast Scarlet B (ICI) ... ... | — | 10 | 12 | 0 | 5 |
| (9) | Coomassie Red R (ICI) ... ... | — | 10 | 12 | 6 | 4 |
| (10) | Durazol Red 2B (ICI) ... ... | — | 16 | 18 | 2 | 15 |
| (11) | Kiton Red 6B (CAC) ... ... ... | 57 | 18 | 15 | 4 | 22 |
| (12) | Alizarine Fast Violet R (CAC) ... | 1073 | 3 | 5 | 3 | 6 |
| (13) | Diphenyl Violet BV (Gy) ... ... | 394 | 10 | 12 | 10 | 15 |
| (14) | Disulphine Blue FF (ICI) ... ... | — | 10 | 12 | 3 | 3 |
| (15) | Solacet Fast Blue 2B (ICI) ... ... | — | 4 | 5 | 7 | 2 |
| (16) | Anthraquinone Violet (CAC) ... ... | 1080 | 4 | 5 | 0 | 7 |
| (17) | Solway Blue A (ICI) ... ... ... | — | 17 | 20 | 2 | 12 |
| (18) | Solacet Navy Blue G (ICI) ... ... | — | 6 | 5 | 20 | 18 |
| (19) | Coomassie Navy Blue G (ICI) ... | 289 | 10 | 15 | 12 | 16 |
| (20) | Durazol Blue 2R (ICI) ... ... | — | 10 | 10 | 20 | 25 |
| (21) | Solway Blue B (ICI) ... ... ... | 1054 | 18 | 20 | 7 | 10 |
| (22) | Disperse acetate rayon dyes ... ... | — | 3 | 5 | 0 | 0 |
| (23) | Chlorazol Hosiery Brown BV (ICI) ... | — | 10 | 15 | 11 | 30 |

estimations using yarns possessing different amine end-group contents, produced by differences in raw material and by acetylation. In another experiment, designed to test the hydrogen bonding theory of disperse dye–nylon combination, the uptakes of a disperse dye from organic media were compared with the changes in length of undrawn yarn produced by phenol in the same solvents. Phenol is also believed to hydrogen-bond to nylon. Apart from water, agreement between uptake and activity of phenol is reasonably good.

The interest in all these problems is not solely academic. The present work was designed primarily to help in the production of nylon, but it is of considerable value to the dyer, too. In the same way, better understanding of the mechanisms of dyeing would gratify the experimenter and lead to the development of new dyes and dyeing techniques to give improved dyeings. Whilst considerable refinement in present techniques of dyeing is possible and desirable, fundamental work may introduce new concepts and give rise to unexpected, but long sought improvements. Yarns could be "tailored" to fit the dyes, and dyes and their modes of application could be made to suit the yarns.

* * *

The author wishes to thank the Directors of British Nylon Spinners Ltd. for permission to publish this paper, and also to acknowledge many helpful discussions with colleagues.

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## Discussion

Mr. B. KRAMRISCH: Wool dyes are of importance in the dyeing of continuous-filament nylon, as they fill certain gaps, especially with regard to certain hues which cannot be obtained with disperse acetate dyes, and also in many cases offer advantages in wet fastness, such as fastness to washing. Wool dyes, however, exhibit certain defects, such as levelling difficulties due to lower migration as compared with the same dye on wool[9]. They also give rise to difficulties in compatibility in certain combination shades and show up yarn irregularities. In connection with the classification of anionic dyes, can any deductions be made regarding the actual dyes, with respect to chemical grouping, molecular weight, and degree of sulphonation?

Mr. PALMER: The relation between molecular constitution of dyes and their sensitivity to differences in amine end-group content is fairly

well defined. Dyes of low molecular weight and low degrees of sulphonation are less sensitive to amine end-group content than similar dyes of higher degrees of sulphonation. The sensitivity of dyeing rate to differences in fine physical structure is less easily related to constitution. Generally, the larger and more complex dye molecules containing three or more sulphonic acid groups are most sensitive to differences in fine physical structure. Apparently anomalous behaviour is all too frequent, however.

Mr. R. J. HANNAY: A recent patent [10] claims that discharge effects may be produced by printing nylon, which has been dyed with selected acid dyes, with other dyes or colourless substances which have a greater affinity for the nylon than the original dye. It would be interesting to know whether the dyes used for the original ground shade in this process all fall within the author's category of uneven dyeing types.

Mr. PALMER: The ground shade dyes are presumably the uneven dyeing types and the displacement dyes the even dyeing. The relation between displacement behaviour and level dyeing behaviour has not been examined.

Mr. A. S. FERN: It should be possible to predict from its structure into which class (for covering nylon of variable quality) a dye falls. Thus it would be expected that Class A dyes are all high-affinity monobasic dyes, Class B polybasic (2 or 3 $SO_3^-$) acid dyes, and perhaps the simpler "direct" dyes and Class C highly sulphonated ($> 3$ $SO_3^-$) "direct" dyes of comparatively great complexity and length. There will probably be anomalies, but it would be interesting to hear to what extent practical knowledge confirms these predictions.

Mr. PALMER: Dyeing behaviour can be predicted broadly from fundamental concepts such as dye constitution and free energy changes during dyeing. The goal of the dyemaker and research worker must be the establishment of this type of relationship, but there is a place, too, for the more empirical type of approach, such as that suggested for the classification of anionic dyes.

Mr. FERN: The technique for obtaining replacement of one dye on nylon by another during printing is a direct extension of one of the methods (the competition method) used for measuring the affinity of acid dyes on wool [11].

Mr. J. V. SUMMERSGILL: In Fig. 1 no actual time is given, but it is stated that with an anionic dye several hours are required to reach point *C*. Are there any anionic dyes which attain point *C* after a normal dyeing time? Furthermore, do the anionic dyes show sufficient variation in the time at which *C* is reached to produce differences in hue when dyeing mixture shades?

Mr. PALMER: No anionic dye examined reaches *C* after a normal dyeing time. Hue differences could certainly result from differences in degree of order when dyeing with mixtures of dyes, because of differences in the sensitivity of individual dyeing rates to degree of order. However, the problem is less acute than the general one of compatibility, introduced by the small number of dyeing sites in nylon.

Mr. C. L. BIRD: Uneven-dyeing ("barry") viscose rayon is the result of physical variations in the yarn, e.g. varying degrees of orientation. Is the same phenomenon in nylon due almost entirely to chemical causes, viz. to variation in amine end-group content?

Mr. PALMER: Chemical variations are at present the most serious source of uneven dyeing in nylon. The phenomenon is presumably caused by the small number of dyeing sites in nylon compared with other natural and synthetic fibres. The reason for the relative unimportance of differences in fine physical structure is probably the flexibility of the nylon chain molecules and the mode of ordering of these chains.

Mr. J. BOULTON: What, precisely, is the fine-structural feature which gives rise to differences in light reflectivity along the length of a nylon filament?

Mr. PALMER: The reason for the present variations in light-reflecting properties is not clear. It is possible to produce gross differences artificially by variations in, say, crystallite size. However, it is not safe to conclude from these experiments that variations in production yarns are of this type, since a technique sufficiently sensitive to characterise the smaller differences between the molecular structures of production yarns is not available.

Mr. H. R. HADFIELD: Is additional detailed information available on those dyes which cover differences in amine end-group content of the nylon? In the detailed results (Fig. 2 and 3) it is shown that differences in amine end-group content cause differences in (*a*) rate of dyeing and (*b*) final dye uptake. As far as dye uptake is concerned, with the three dyes examined, differences due to amine end-group content cause variations in dye uptake. Later the author suggests that certain anionic dyes will cover such amine differences. Has he examined these particular dyes in detail by the techniques used to obtain the results in Fig. 2 and 3? Such results would prove most interesting, in that time of half-dyeing and uptake of dye should be practically independent of amine end-groups— a result not hitherto observed.

Mr. PALMER: Perhaps the use of the word "cover" is misleading. The intention was not to suggest that no differences in dye content would exist between yarns of different amine end-group content, but to imply that the differences in dye content would be too small to be detectable visually. Unfortunately, there is no further detailed information, such as that in Fig. 2 and 3, for the other dyes in Table I.

Dr. H. R. HIRSBRUNNER: It has been shown that the adsorption of ordinary acid dyes on nylon can be explained on the assumption that dye ion adsorption occurs directly on positively charged amine groups in the fibre; but in the case of acid milling dyes there are discrepancies which suggest that other methods of attachment may operate, such as adsorption of the dye acid upon amide groups. Another suggestion is that the discrepancies are due solely to the fission of peptide bonds which occurs at low pH values, in other

words to an increase of amine groups in the nylon molecule. This point has been stressed lately by American workers. Is there any experimental evidence which would shed light on this problem?

Mr. PALMER: The point raised is one of great theoretical importance. We have done a little work on the problem, but have not been able to reach any definite conclusions or put forward new ideas. The major problem is that individual dyes vary enormously in behaviour, particularly at low pH values. Our work has included (1) measurement of free energy changes during dyeing, (2) dyeing of undyed nylon and nylon which has been desorbed after dyeing at a low pH, (3) examination of the physical properties of dyed yarns, and (4) measurement of relative viscosity. The work suggests that at low pH values a compromise between the views of Remington [12] and of Vickerstaff [13] is necessary. The amount of hydrolysis is greater in the presence of dye; but it is not sufficient to account for the extra dye absorbed, since on desorption and redyeing at a higher pH, the same amount of dye is not absorbed by the yarn as at the lower pH. One point is that the use of solution viscosity for the characterisation of chain length appears to be very difficult with nylon. This same work on nylon solutions shows that the amide groups of nylon in solution readily accept protons and that anions can act as gegenions to these protons.

No relation is apparent in our results between the amount of dye absorbed and the change in physical properties on dyeing at low pH values. This result is, perhaps, not too serious from the point of view of dyeing theory, since our knowledge of the mechanism of extension of both drawn and undrawn yarn is so meagre and the published ideas on the subject seem to need modification.

For those dyes which apparently combine with the peptide link as well as with the amine end-group at normal pH values, there is very little to add apart from the fact that the dyeing properties of *N*-substituted polymers are very similar to those of normal 66 nylon. However, it is not easy to relate the results because of differences in amine end-group content and in fine physical structure between the various polymers.

The easiest way to view the dyeing properties of these dyes is to consider the free energy changes during dyeing. A possible additional mode of attack on the problem might be the measurement of free energy changes during dissolution.

Mr. C. P. TATTERSFIELD: The tendency to classify dyes for application to a particular fibre as A, B, and C will eventually lead to confusion. Dyes such as Red F and Chrysophenine are applied to different fibres, and might therefore come in different classes depending on the fibre being considered. Would it not be helpful to preface the letters A, B, C, etc. by some other letter? For example, in the case of the classification in § 6 of this paper, refer to classes NA, NB, and NC.

Mr. PALMER: Confusion will undoubtedly arise if we have any more A, B, C classifications. However, the scheme proposed is only tentative, and the nomenclature can easily be decided.

Mr. C. J. WRIGHT*: Much has been said about variation in light reflection and its ultimate effect in causing dyeing unlevelness. The same effect often occurs with, for example, mercerised cotton, and in both cases may be due to irregularity in crystalline alignment and corresponding variations in the amorphous regions within the fibre structure. This must, therefore, affect the uptake on to and diffusion into the fibre of the dye from the dyebath. The provision of controlled conditions in the manufacture of synthetic fibres to promote sufficient amorphous regions is a pressing problem, in order to assist the colourist, whether dye application is via aqueous or solvent medium. To this should be added the stimulus of organic colour chemistry, with a view to producing dyes capable of dyeing, not merely colouring, highly crystalline fibres.

Mr. PALMER*: The lustre differences we have to contend with are undoubtedly related to differences in fine structure. As to the production of a synthetic yarn which dyes easily, there seem to be two points to be remembered. Firstly, a strong yarn must have a highly ordered structure. Secondly, the proportion of amorphous regions and amount of moisture absorption are probably not the only factors governing the entry of dyes into a fibre. The large difference between the influence on dyeing rates of molecular orientation in nylon and in viscose rayon illustrates this last point.

* Communicated

# Developments in the Application of Dyes to Cellulose Acetate Rayon

A. Mellor and H. C. Olpin

The disperse dyes are likely to remain the principal dyes for acetate rayon, particularly for piece dyeing. The "duosol" dyes are unlikely to supersede them for general purposes, but are likely to increase in importance with expanding use of acetate staple fibre. The azoic dyes, applied by the "concurrent" method, supplement the above groups for specific shade requirements such as fiery scarlets and deep rich wines, and in addition are fast to wet processing. Solvent dyeing as an economic step has achieved some measure of success, chiefly in America, but the application of vat dyes by such techniques still remains a problem which is very much for the expert.

For printing acetate rayon goods the disperse dyes, though much used, suffer from inherent processing and fastness defects, and it is desirable to replace them by the "duosol" and acid dyes for normal requirements. Selected vat dyes may also be applied very satisfactorily. The use of swelling agents, e.g. the thiocyanates and water-soluble polar solvents such as ethyl lactate, offers great scope for prints of improved beauty and fastness, and in certain cases permits elimination of the steaming operation.

## Introduction and Early History

A textile fibre which cannot be dyed readily suffers extreme disadvantage in the textile industry. It is not surprising, therefore, that as soon as a new synthetic fibre is made, and long before it is in economic production, its sponsors are concerned to determine its dyeing characteristics. The history of the dyeing of acetate rayon dates back to the beginning of the present century, and it is evident from the literature that the early investigators were experiencing difficulty in achieving satisfactory colorations with the dyes then available. Thus dyeing with acid, substantive, and basic dyes in such mixtures as aqueous methylated spirit, aqueous acetone, and aqueous acetic acid was suggested in a patent as early as 1906[1]. Later patents[2] proposed preswelling treatments with these solvent mixtures or with amines, phenols, or other organic substances or with aqueous solutions of these, and also with aqueous inorganic acids, following which the yarn or fabric was dyed in the ordinary manner. These patents also disclose that the amines or phenols in the fibres may be converted into dyes by appropriate treatment, e.g. amines into azo dyes by diazotising and coupling with end components. Mork[3] proposed an incomplete saponification of cellulose acetate to impart affinity for otherwise ineffective dyes. It is probable that these early workers were experimenting with the triacetate, which is more resistant to water-soluble dyes generally than the present "secondary" acetate. Nevertheless the dyeing prospects for even the "secondary" acetate yarns were more or less unsatisfactory when the Dreyfus brothers successfully produced and marketed Celanese acetate rayon in the years immediately succeeding the first World War. The appearance of this rayon of secondary acetate greatly stimulated research into methods for dyeing it, and for dyes which would dye it by conventional processes. Saponification to regenerate the original cellulose was tried, but in the main soon abandoned. Nor did an early proposal[4] to use the thiocyanates to swell the fibre, either as a separate treatment before dyeing or by addition to the dyebath, afford a permanent solution to the difficulties. The work is, however, of special interest in view of more recent developments in this field. An interesting and authoritative review of the position in 1921 was given before the Society on 20th October 1921 by J. F. Briggs[5]. Both saponification and swelling techniques were discussed, but emphasis was placed on direct dyeing methods, and the conviction expressed that, as the demand developed, dyemakers would bring forward new dyes especially designed for this new fibre. In exploring the techniques used for the older fibres mordanting and weighting were also attempted, British Dyestuffs Corpn.[6] applying chromium, aluminium, and iron mordants by way of their benzoates, salicylates, and especially their thiocyanates, whilst British Celanese Ltd. and others[7], working on similar lines, were able not only to apply sufficient metal for mordanting purposes, but were even able to imitate the weighting of natural silk with tin salts. Such processes were designed to apply the available water-soluble dyes, particularly the direct cotton dyes, to acetate, but were fraught with peculiar difficulties. Meanwhile there appeared an array of water-soluble dyes which were serviceable on the secondary acetate and could be applied by conventional methods. These were doubtless selected by the simple procedure of trial and error, as many of them were established commercial dyes. Others were old products which had not previously been used commercially, and still others were new[8]. They appeared in such ranges as the Cellit Fast (IG), Cellutyl (BDC), Setacyl (Gy), and Acetate (A) dyes.

This introduction would not be complete without mention of the Ionamines, introduced by British Dyestuffs Corpn. (B.D.C.) in 1922[9], which were *N*-sulphomethyl compounds (*N*-methanesulphonic acids) derived from the primary and secondary amino groups of otherwise insoluble dyes. The essential technique of solubilisation imposed severe limitations, and the Ionamines were soon found to be unnecessary, being superseded by the now universally accepted disperse dyes, of which, broadly speaking, they were derivatives.

Before the disperse dyes were fully established, however, B.D.C.[10] made a further and lasting contribution by their discovery that many dyes of simple structure containing an external sulphato group, of general formula $R^1{\cdot}NH{\cdot}C_2H_4{\cdot}O{\cdot}SO_3Na$

or $R^1{\cdot}NR^2{\cdot}C_2H_4{\cdot}O{\cdot}SO_3Na$, had good substantivity for the fibre. These dyes were of a type discovered a year or two earlier by Green and Saunders[11] but not described by them as suitable for acetate rayon. They were, however, overshadowed at the time by the development of the disperse dyes and were not offered to dyers until more than a decade later, when some of them appeared, together with other dyes of rather different types, in the Solacet (ICI) range of water-soluble dyes for acetate rayon.

It should also be mentioned that the unique dyeing properties of acetate rayon enabled resist or cross-dyed effects to be produced in the presence of other fibres, and that such possibilities were exploited at a very early date, and have continued to exert an important influence on the textile industry.

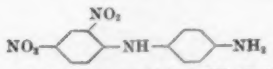
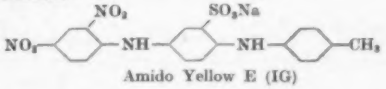
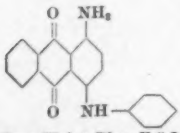
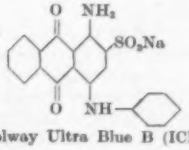
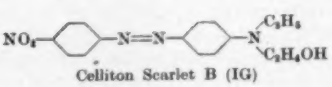
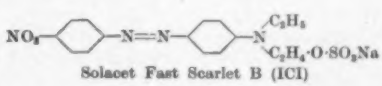
The major proportion of acetate rayon is dyed to-day with disperse dyes, by which term are understood dyes which, while having affinity for the fibre, are for all practical purposes insoluble in water and so are applied to the fibre from aqueous dispersions. It is interesting to note the active part played in their introduction and development by those immediately interested in the dyeing of this new fibre, including of course the makers of acetate rayon themselves, who could not afford to wait for routine developments in the dyemaking industry. Holland Ellis of British Celanese Ltd. was the first to recognise the possibilities of the simple water-insoluble azo dyes and to devise a satisfactory way of applying them, namely to pretreat them with Turkey Red oil or other sulphated fatty acid before addition to the dyebath[12]. Very quickly he extended the method to other classes of insoluble dyes, and showed that the sulphated fatty acids could be replaced by soaps and similar bodies. Simultaneously Baddiley and Shepherdson of B.D.C. filed a patent application[13] covering the dyeing of acetate rayon with simple amino derivatives of anthraquinone, while a little later Hall, of the Silver Springs Bleaching & Dyeing Co.[14], realised the possibilities of the nitrodiarylamines.

Holland Ellis not only played a leading part in the development of the disperse dyes as we know them to-day, but, essentially a dyer, was also responsible for establishing in the dyeing industry the "disperse" technique, which is comparable in ease and simplicity with the application of the substantive dyes to cotton.

The dyeing of acetate rayon from aqueous dyebaths therefore soon became the established technique, so much so that C. E. Mullin[15] in his book *Acetate Silk and its Dyes*, published in 1928, begins a short chapter on "Swelling Agents or Solvents in Dyeing Acetate Silk" with the words: "Without doubt all of these solvent methods of dyeing acetate silk are now obsolete", and most dyers at that time would have agreed with him. But, as we shall see, interest in the solvent dyeing technique never quite flickered out, and in little more than a decade there was a revival of interest in an endeavour to solve some of the problems in the dyeing and coloration of acetate rayon which had not yielded to more orthodox methods.

## THE DISPERSE AND "DUOSOL" DYES IN DYEING

The term "disperse" dyes has already been discussed in this paper; the term "duosol" dyes has been coined to describe their counterparts, mainly sulphonated or sulphated dyes, which are soluble both in water and in organic solvents and are substantive to acetate rayon from aqueous dyebaths. They have been marketed under the trade names Solacet (ICI) and Cellit (IG), and doubtless other series of such dyes will appear in due course. Individual dyes of the duosol type, such as Amido Yellow E (*Colour Index*, No. 11), Solway Ultra Blue B (ICI), and Chlorazol Fast Orange G (ICI) are also to be found scattered in the various acid and direct cotton dye ranges. The similarity in structure of the disperse and duosol types may be illustrated by the following examples—

| Disperse Dyes | Duosol Dyes |
|---|---|
| NITRODIARYLAMINE | |
|  |  |
| S.R.A. Golden Yellow IX (BrC) | Amido Yellow E (IG) |
| ANTHRAQUINONE | |
|  |  |
| S.R.A. Fast Violet Blue F.S.I. (BrC) | Solway Ultra Blue B (ICI) |
| AZO | |
|  |  |
| Celliton Scarlet B (IG) | Solacet Fast Scarlet B (ICI) |

The disperse and duosol dyes in general have similar fastness properties, a point of considerable theoretical interest in view of the presence of the sulpho groups. But in spite of the advantage of water-solubility the duosols are not in general use, being mainly restricted to pale shades. The reason lies in the very important fact that they are much more sensitive to slight variations in physical characteristics of the individual threads, so that stripiness due to selective absorption is often very apparent, whereas the same shade dyed on the same warp with disperse dyes is usually free from this fault. However, the duosol group is of considerable interest in dyeing acetate staple fibre in all its forms, whether loose stock, slubbing, yarn, or fabric, since the textile operations ensure blending of the fibres, and the above consideration becomes of secondary importance. Being essentially acid dyes and having preferential affinity for wool, they are not suitable for acetate staple–wool mixtures, for which disperse dyes are quite satisfactory [16]. It is a matter of interest that, so far as the authors are aware, no duosol base suitable for diazotising and coupling has yet appeared.

The disperse dyes are used to-day for dyeing most fabrics in which acetate rayon yarns appear, e.g. all-acetate outerwear and underwear fabrics, and the acetate component of mixture fabrics. It is also of interest that dyes of this class having the necessary fastness to light are available for furnishing purposes [17], and have been used continuously on Celanese furnishing fabrics for many years. A considerable weight of continuous-filament yarn is dyed also in yarn form with disperse dyes for special purposes.

Imperfections of both fastness and dyeing properties are well known to be present, but in spite of the obvious need for improvement progress is slow. The reason is not far to seek. The limitations imposed by the fibre itself preclude the use of large dye molecules. Vickerstaff [18] gives the probable diameter of the capillaries of acetate rayon as about 10 A., which does not leave much room for accommodating large dye molecules. Whether these capillaries exist as rigid entities, or whether solid solution in the randomly orientated regions of the fibre is a more profitable concept, is still debatable. It is certain, however, that solubility in organic esters such as ethyl acetate is a valuable guide to the probable behaviour of a dye towards acetate rayon.

Azo, nitrodiarylamine, and anthraquinone are not the only chromogens which have yielded good results. Other interesting examples are—

(1) BENZANTHRONE [19]— 3-Methoxybenzanthrone is an intensely fluorescent yellow, marketed as Duranol Brilliant Yellow 6G (ICI). This contains no nitrogen.

(2) *peri*-NAPHTHALIMIDE [20]— Celliton Brilliant Yellow FF (IG) is the imide obtained by condensing *m*-xylidine with 4-amino-1:8-naphthalic anhydride.

(3) NAPHTHAQUINONE and NAPHTHAQUINONEIMINE — The Geigy Co. have described [21] the production of bright green–blue dyes by the reaction of a naphthazarin intermediate with a primary aromatic amine, in particular *p*-phenetidine. More recently the Sandoz Co. have taken out a series of patents [22] in which they show that certain of the halogen atoms in di-, tri-, and tetra-halogeno derivatives of naphthaquinone-imines are labile, and are replaceable by other groups to give blue dyes for acetate rayon. It has been suggested [23] that the recently introduced Artisil Direct Blue GFL (S) is of this type. If so, its excellent fastness to atmospheric fumes is remarkable, meriting elucidation from the theoretical standpoint.

### AZOIC AND VAT DYES IN AQUEOUS DYEING

The use of acetate rayon effect threads prompted enquiry for dyed yarns which would be fast to textile dyeing processes. The disperse and duosol dyes are not satisfactory for this purpose, for which colours of the fastness associated with the azoic and vat dyes on cellulose fibres are desirable. Both the latter types can, however, be incorporated as pigments in the spinning solution, and together with the phthalocyanine pigments give a range of shades which is at least equal in all-round fastness properties to that obtainable on any other fibre. Acetate yarns are at present produced in a wide variety of yarn and filament deniers and also in different lustres, and a moment's contemplation of the problem involved if each were required to be mass-dyed in a multiplicity of shades to give the exact effect required by the customer *on the finished goods* will show how impossible this would be. Their production in bulk, therefore, must necessarily be restricted to a comparatively small range of shades and yarn qualities.

It is possible, however, to apply many azoic combinations to acetate by the "concurrent" method, and a number of indigoid and a few anthraquinonoid vat dyes may be applied as the free leuco compounds. Their application and properties were discussed by the present authors in 1947 [17], since when the range has not substantially increased. The fullness and richness of shade of some of these azoic combinations is a valuable asset in itself, and on many occasions they have been used in ordinary piece dyeing to obtain colours unobtainable by other means. In the nascent state they are doubtless molecularly dispersed, and their true shade and maximum fastness properties are developed only under physical conditions, such as soaping or steaming, which induce aggregation. They vary widely among themselves in this respect, but if migration to the surface occurs, looseness to rubbing results. Aggregation must therefore be carried only far enough to ensure reasonable stability. No hard and fast rule can be given, since some, e.g. Fast Red RC Base→Naphtol AS–LB, change enormously in hue during aggregation, whilst others, e.g. Fast Scarlet GG Base→Naphtol AS–LB, show little change but the light fastness is greatly improved.

### SOLVENT-SWELLING METHODS IN DYEING

In the dyeing industry research may be divided into two categories, namely investigations which are concerned with improvements in the art to

satisfy specific requirements, and those which are essentially economic in outlook, seeking to find shorter and cheaper or better methods of applying dyes of known fastness. If both objectives can be achieved at the same time, so much the better, and both can be detected in the history of the dyeing of acetate rayon by swelling techniques.

Continuous-filament acetate yarn has always presented manipulative problems, being still dyed mainly in hank form in spite of the costly textile operations involved in hanking and rewinding. Some degradation in yarn quality or difficulty in rewinding occurs no matter how carefully the dyeing operation is carried out. In the past the disperse dyes presented great difficulties in package dyeing, filtering out readily in the first few layers of yarn, to give very unsatisfactory results. Recently, however, progress has been made in the cheese dyeing of continuous-filament yarns by paying due attention to such points as winding tensions, winding pattern, choice of dyebath ancillaries, and choice of dyes. To-day suitably wound acetate rayon cheeses can be dyed successfully with duosol dyes, azoic combinations, and the more soluble disperse dyes. Meanwhile, however, other methods have been tried, including passing the yarn from bobbin to bobbin through a solution of the dye in a volatile organic solvent mixture which is also a swelling agent for the fibre, and drying in. If the volatile solvents could be recovered, a dyeing process with economic possibilities seemed assured. Such a process was in fact evolved [24], a typical procedure being to pass the yarn through a 0·25% solution of a disperse dye, e.g. 1-hydroxy-4-aminoanthraquinone, in a mixture of 40 parts of ethyl acetate, 60 parts of ethyl alcohol, and 20 parts of water, and then to dry it by passing through air at 40°C. It is quite successful for pale shades, but difficulties arise when medium to full shades are desired, for surface deposition of dye may occur by evaporation before penetration of the fibre is complete.

Some of the earliest attempts at dyeing woven fabrics in solvent systems visualised circulating the liquor through the fabric [25]. The dyes used were of the disperse type, dissolved in solvents such as the alcohols, the aromatic hydrocarbons, and the more volatile chlorinated solvents such as di- and tri-chloroethylene. A further development was the use of aqueous di- or poly-hydric alcohols or their ethers or esters [26], in which the disperse dye was dissolved, the solution being padded on to the fabric to give the required coloration. The process was adaptable to yarn dyeing, for travelling yarns could be passed over a wick saturated in such a solution [27], enough dye being thereby picked up for adequate coloration.

Rapid dyeing of piece goods of acetate rayon was also attempted by passing the fabric in full width through a solution of the dye in a solvent such as dichloroethylene and drying [28]. In order to assist full development of the colour it was found to be beneficial, after padding, to run the goods through a chamber containing air saturated with solvent vapours, thereby avoiding evaporation of the fairly volatile solvent during the fixing process. A typical procedure was to dissolve a dye such as α-methylaminoanthraquinone in dichloroethylene, pad the solution on to the fabric, the nip being adjusted to give a 75% uptake of dye liquor, and give a 10-sec. passage through an atmosphere saturated with dichloroethylene before drying in a chamber from which the solvent vapours could be recovered.

As the patent literature of the 1930s will testify, the possibilities of increasing the receptivity of the acetate rayon fibre for dye by swelling were once more beginning to be realised by many workers, both in this country and in America, and observations enabled certain general principles to be formulated. Since the organic solvent is to be used in a wide range of concentrations, say 20–80%, it must be cheap. It must also be water-soluble, since water is the cheapest diluent, and in our experience a very desirable ingredient in solvent dyeing mixtures. The organic solvent must be non-poisonous, non-dermatitic, and a solvent for the dye. Recovery of the solvent may be visualised, as in one or two of the processes discussed above, but the general tendency is to consider the solvent thus used as lost, regarding it as a cost against which must be set gains in processing time, in the use of cheaper dyes, in fastness properties of the colorations achieved, and so on. It would be most difficult to attempt to summarise the patent literature in this field, but it is true to state that reawakening to the possibilities of solvent dyeing from the economic angle was most evident in America, where the Celanese Corpn. of America did much work, as also did the Atlantic Rayon Corpn. The Sandoz Corpn. of America suggested the use of neutral aqueous alcoholic solutions, selecting acid dyes and possibly also certain direct cotton dyes which could be applied in this manner, and marketing them in concentrated form as the Artol dyes. Among them is Artol Blue B, a dye which is remarkable both for its dyeing properties and for its fastness on acetate rayon. Its excellent fastness to burnt gas fumes merits special mention.

The Celanese Corpn. of America [29] showed that it was possible to employ a padding technique, using either disperse or acid dyes dissolved in aqueous alcohol of 70–80% strength. After 6 sec. immersion the fabric was squeezed through the padding rollers and passed into a drying chamber at 95°C. After drying it was of course necessary to wash off and finish as usual. Shade standardisation by this process was rather uncertain, and topping to shade as a separate dyeing operation was practised [30]. Nevertheless, considerable saving in time was effected, and the process was proved to be economically effective, so much so that millions of yards of fabric have been thus dyed. The disperse dyes were preferred to the acid dyes, probably on account of the appearance of warp streaks when the latter were used. A little later [31] it was shown that thiocyanates were useful additions to alcohol–water dye liquors for disperse, acid, and leuco vat ester dyes, and also that useful colorations could be obtained even if washed off prior to drying.

The Atlantic Rayon Corpn. and Textron Inc. give, in a series of patents [33], a wealth of data on

the application of acid dyes to acetate rayon from swelling baths of high acidity. The first of these patents uses aqueous formic and/or acetic acid adjusted to pH 1·4 with mineral acid. This was subsequently modified to pH 2·23 or below, and polyhydric alcohols and their ethers and esters were introduced. Warp streaks were, however, still troublesome, and it was claimed that these could be eliminated by releasing stresses and strains by a preliminary run in a blank dyebath.

At Spondon we have carried out a considerable amount of work on this subject, and have reached definite conclusions. An important point is that the normal processing treatments given before aqueous dyeing, such as steeping and scouring, may require modification for solvent dyeing. This may be shown very easily in the laboratory by taking two squares from the same warp satin fabric and scouring at 60°C. and 85°C. in a conventional scouring bath. After drying, both are dyed by immersion for a few minutes in a dyebath made up of 75 parts methylated spirit, 25 parts water, 2 parts ammonium thiocyanate, and 0·2 part of a suitable acid dye at 25°C. After immersion both are washed off and dried. The fabric scoured at 85°C. is considerably weaker in shade. During the dyeing it will also be noticed that in both fabrics warp streaks are very prominent on first immersing in the dyebath, but are slowly eliminated, till a satisfactory result is eventually obtained.

It is also a matter of considerable importance that washing-off conditions can influence both colour yield and warp stripiness. Drying-in is not always a desirable operation, and many dyes wash out badly in water. We have found, however, that the presence of an electrolyte is very beneficial in many cases[33], a particular instance being that of Xylene Fast Green B, which, in the absence of electrolyte, can be completely washed away before aggregation and/or reduction of pore size inhibits further loss of dye.

When water-soluble dyes are used, whether acid dyes, premetallised acid dyes, or leuco vat esters, a minimum processing time is essential if results comparable in levelness with those obtained by normal disperse dyeing methods are to be achieved. It is also essential, of course, always to bear in mind that the fabric is in a swollen and fully relaxed condition, and will tend to shrink. If excessive warp tension is applied, however, there will be grave danger of the plastic fabric being permanently stretched and impoverished in appearance. A balance must therefore be struck between the various contending factors. Dyeing temperatures may vary considerably, the same result being obtained by dyeing cold in a more concentrated solvent mixture as would be obtained warm by the use of a less concentrated mixture.

This technique is applicable to acid, premetallised acid, and basic dyes, and has been extended to the vat dyes, which will now be considered.

### DYEING VAT DYES BY SOLVENT-SWELLING METHODS

Many attempts have been made to apply vat dyes to acetate rayon. As stated earlier in this paper, the free leuco compounds of many indigoid dyes, and of a few anthraquinone vat dyes, have affinity for the fibre. Among these, particular mention must be made of the brominated indigos, Alizarin Indigo 7R, and Caledon Jade Green XS. These have been particularly welcome for yarn dyeing for fancy effects, but this technique does not give the range of shades required on piece goods such as furnishings. Many methods were proposed, which may roughly be divided into those depending on true dyeing technique, and those depending on mechanical application of the dye plus other ingredients, followed by drying and steaming in a manner analogous to that employed in textile printing. It may naturally be inferred that any printing technique which gives successful results may be turned into what is in effect a dyeing process by reducing the viscosity of the print paste and resorting to padding methods of application; and, as will be seen in the Printing section of this review, many vat dyes may be so applied to acetate rayon.

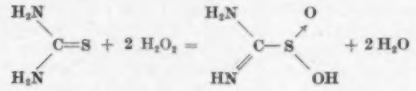
Success with the sulphonated dyes by solvent dyeing techniques naturally turned attention to the vat ester dyes, which are sulphato esters of the enolic leuco compounds. They have good affinity for the fibre from such dyebaths as 60:40:4 methylated spirit–water–ammonium thiocyanate mixtures. Cellulose fibres present, e.g. cotton and viscose, are resisted very satisfactorily, enabling cross-dyeings to be made, provided that the cellulose fibre is cleared of leuco ester, by soaping if necessary, before oxidation.

The anthraquinone vat dyes proper (as contrasted with the leuco vat esters) have been the subject of much work, both here and in America, using dyeing, padding, and printing techniques. G. D. Sutton, associated with the firm of T. E. Marchington & Co. Ltd., states for example[34] that if a weaker alkali than a caustic alkali, such as ammonia, triethanolamine, or sodium carbonate, is used in vatting, or even if caustic alkali is used and all excess removed before dyeing, a liquid organic swelling agent also being present, very strong coloration of cellulose acetate is obtained in a relatively short time (5–10 min.) and at comparatively low temperature (25–40°C.), with little or no saponification of the cellulose acetate rayon. Conditions are such that considerable swelling takes place, and better results are obtained when the fabric is not under tension. A typical procedure is to vat the dye, e.g. Caledon Jade Green 4GP, in water with caustic soda and hydrosulphite at 50°C., add sodium bicarbonate to the bath in order to convert residual caustic soda into sodium carbonate, and then add ethyl alcohol till the composition of the bath is about 70% alcohol. On dyeing for 10 min. a jade green shade results, cellulose fibres present being substantially undyed. In other examples ammonia, triethanolamine, and other alkalis are used. Satisfactory colorations are given by such dyes as Caledon—

| | |
|---|---|
| Yellow 3G | Blue RN |
| Brilliant Red 3B | Brilliant Orange 6R |
| Jade Green 4GP | Red Violet 2RN |

One example of the above patent proposes to pad the unreduced dye on to the fibre, dry, and then pass into a dyebath such as is described above. Reduction and fixation then take place with very little bleeding off into the dyebath.

In a further effort to suit the process to the fibre Sutton[35] has worked with an organic reducing agent, namely formamidinesulphinic acid, obtained very readily by interaction of thiourea and hydrogen peroxide—



In other respects the procedure is essentially as described above.

In processes such as these, cellulose fibres present are surprisingly little stained, so that they can subsequently be cross-dyed with the same or different vat dyes to give solid or contrasting effects. Though much progress has been made, the processes so far evolved demand much expert supervision.

### PRINTING

In general, acetate rayon can be printed with those dyes which have direct affinity for the fibre, while, since there always appears to be room in printing pastes for another ingredient, swelling agents and other assistants may be applied and operated under full control to fix a wide range of dyes not normally used in dyeing.

For application printing the most widely used are the disperse dyes. Their insolubility in the printing paste appears to be advantageous rather than otherwise, since no problems of dye separation arise as is so often the case with water-soluble dyes. It is important that only those disperse dyes be selected which are non-volatile, otherwise trouble is bound to occur owing either to direct marking off during steaming or to slow impregnation of back-greys. Another reason is that volatile dyes are liable to mark off during storage of the finished goods, and once this has happened the reclamation value of the fabric is almost negligible. But even with the best selection of dyes, and the most careful handling, there is always a danger of the white ground or very pale shades being stained during washing-off by unfixed dye from the heavy shades, for dye fixation in the latter is never complete. After steaming, therefore, washing off should be carried out in open width using as much water as possible, and under no circumstances should the goods be left lying in a wet condition. The disperse dyes are often printed without any assistants, but additions of up to 10% of solvents such as methylated spirit, thiodiglycol, or ethyl lactate may be made to assist penetration and ensure good colour yield. A finely comminuted dye paste free from aggregates of particles is essential, and close study of this requirement will be amply repaid if clear pastel shades free from dye-specks are to be obtained. Tertiary shades are obtained by mixing, and even blacks are obtainable, but often the latter are considered too great a hazard, and oxidation blacks are used.

The duosol dyes offer several advantages over the disperse dyes in that they are non-volatile and are far easier to wash off owing to their water-solubility and lack of affinity for the fibre under normal washing-off conditions. Owing also to this same lack of affinity in the absence of electrolyte, they remain clear and bright after repeated launderings, whilst disperse dye controls, as would be expected, lose their sparkle.

The duosol dyes may be applied from suitably thickened aqueous pastes, but since many are none too soluble, an ancillary such as Solution Salt SV (ICI), which is sodium dibenzylmetanilate, is recommended to inhibit or at least to delay separation of the dye on standing. During the 1930s the possibilities of this type of water-soluble dye attracted the attention of several makers. With so many solvents available, it is not surprising that each maker arrived at a different final recommendation, typical of which are thiodiglycol, triacetin, and resorcinol, either alone or in admixture. Diacetone alcohol and diethyl tartrate are also useful.

A typical recipe is—

| | Parts |
|---|---|
| Dye ... ... ... ... | 3 |
| Thiodiglycol... ... ... | 3 |
| Triacetin ... ... ... | 4 |
| British Gum paste... ... | 55 |
| Water ... ... ... | 35 |
| | 100 |

After printing, the goods are dried, steamed for 40 min. in a festoon steamer, washed off in cold water, and given a light soaping treatment.

A short list of suitable dyes is—

Fast Light Yellow E (LBH)
Cellit Fast Red BB (IG)
Solway Ultra Blue B (ICI)
Setacyl Printing Yellow SG (Gy)
Cellit Fast Violet 4R (IG)

It is a matter of interest that these dyes resist cellulose fibres very well, and any slight staining can be removed by a soaping treatment, so that novel and interesting resist effects can be obtained. However, so far as is known, the style has never been exploited commercially.

The use of swelling agents in quantity sufficient to swell the fibre appreciably admits of the use of dyes of the acid and premetallised acid types. Compatibility with the thickening agent is of course essential, and when working with a 75 : 25 methylated spirits–water mixture it was found necessary to use a methyl cellulose as thickening agent[36]. The use of a small quantity, say 2–4%, of ammonium thiocyanate in these pastes serves the double function of assisting both the peptisation of the methyl cellulose and the fixation of the dye on the fibre.

By the use of aqueous methylated spirit oxidation blacks of great intensity may be achieved [37]. A mixture of *p*-aminodiphenylamine and aniline is used, both of which are very soluble in the thickened aqueous methylated spirit; sodium chlorate is the oxidising agent, and ceric chloride the catalyst. Thus, apart from using aqueous methylated spirit as the printing medium, the recipe closely follows the conventional one for an oxidation black on acetate rayon.

The use of urea as an assistant has also been investigated, because of the disaggregating properties of this compound, and of its great value in the printing of acid dyes on viscose. A simple aqueous paste is used, thickened with gum tragacanth, and containing about 10% urea. It is interesting to note that in general the dyes which are fixed on acetate rayon by this method fall into a group, the "particle size" range of which is smaller than that required for viscose. We have found that the gap between these two groups can be bridged by surface saponification to an acetyl value of 38–40, so that a wide range of dyes becomes available for use [38]. Table I has been adapted from that given by Dr. W. Meitner of the I.C.I. laboratories [39].

TABLE I

| Dye | Particle Size (A.) | | |
|---|---|---|---|
| Naphthalene Fast Orange 2G 120 ... | 4·0 | Applicable to 100% cellulose acetate | Applicable to cuticularly saponified cellulose acetate |
| Tartrazine KS ... | 5·4 | | |
| Azo Geranine 2GS ... | 5·6 | | |
| Lissamine Violet 2RS... | 6·7 | | |
| Naphthalene Scarlet RS | 7·1 | | |
| Carmoisine WS ... | 7·7 | | |
| Acid Magenta AS ... | 8·7 | | |
| Disulphine Blue FFS... | 8·9 | | |
| Naphthalene Red EAS | 12·5 | | |
| Lissamine Red 7BPS... | 12·7 | | |
| Lissamine Green SF 150 | 12·8 | | |
| Coomassie Yellow RP... | 14·0 | | |
| Disulphine Blue A 200 | 14·9 | | |
| Coomassie Milling Scarlet 5BS ... | 16·4 | Applicable to regenerated cellulose, e.g. viscose rayon | |
| Disulphine Green B 150 | 16·8 | | |
| Coomassie Violet R 150 | 20·2 | | |
| Carbolan Crimson BS... | 20·8 | | |
| Coomassie Brilliant Blue FF 200 ... | 22·5 | | |
| Coomassie Brilliant Blue R 250 ... ... | 63·2 | | |
| Carbolan Yellow 3GS... | 66·8 | | |
| Carbolan Violet 2RS ... | 89·1 | | |

Urea is of particular interest in printing the leuco vat ester dyes, improving both the shade and colour yield [40], and since this method may be applied also to dyeing by padding methods the following typical procedure may be of interest—

A pad liquor is prepared of the following composition—

| | Parts |
|---|---|
| Methylated spirit ... ... ... ... | 75 |
| Water ... ... ... ... ... | 25 |
| Urea ... ... ... ... ... ... | 10 |
| Indigosol Golden Yellow IRK (DH) ... | 2 |
| Ammonium thiocyanate ... ... ... | 2 |
| | 114 |

The material is padded at 20–25°C., dried, steamed for two 20-min. periods at 107°C., oxidised in acidified nitrite solution, washed in cold water, soaped at 70°C. for 20 min., and again washed. Further aggregation accompanied by improvement in light fastness may be obtained by a further steaming treatment.

The chrome dyes may also be printed on acetate rayon fabric in much the same way as acid dyes, the chromium acetate being added to the printing paste immediately before printing. The dye enters the fibre, and its chrome lake is formed during the usual steaming operation. Care must, of course, be taken to ensure that conditions are chosen so that the chrome lake is not formed prematurely.

It was noticed at an early date that merely on drying the printed samples a fair degree of fixation of dye took place. This suggested the possibility of shortening the processing time by elimination of the steaming operation. Ethyl lactate has been suggested [41], and further study has shown this solvent in admixture with thiodiglycol to be very effective. 35–40% Ethyl lactate and 6–8% thiodiglycol are necessary, so a methyl cellulose thickener is again used.

Another mixture which has given promising results consists of 5% each of diethyl tartrate, ammonium thiocyanate, and urea.

Table II gives dyes typical of the large number applicable by solvent-swelling methods.

TABLE II

| | Light Fastness |
|---|---|
| Croceine Scarlet 3BS (ICI) ... ... | 4 |
| Aquamine Red EBL (S) ... ... ... | 5–6 |
| Cloth Fast Bordeaux B (CAC) ... ... | 3–4 |
| Cloth Fast Orange G (CAC) ... ... | 5–6 |
| Fullacine Yellow G (CAC) ... ... | 3–4 |
| Aquamine Yellow 2GL (S)... ... ... | 5 |
| Solway Green G 150 (ICI)... ... ... | 5 |
| Brilliant Alizarine Milling Blue FFG (S)... | 5 |
| Brilliant Alizarine Milling Blue 2RL (S) ... | 5 |
| Artol Blue B (S) ... ... ... ... | 5 |

Useful blacks are obtainable with—

(*a*) 1·8% Artol Blue B
1·8% Cloth Fast Orange G
0·75% Fullacine Yellow G

(*b*) 8% Neolan Black WA Extra

but in these cases methylated spirit–water–ammonium thiocyanate gives best results.

The application of vat dyes to acetate rayon lingerie goods has been an established printing style for many years. They are applied from a paste containing Formosul (Br) and soda ash, and steaming conditions are chosen to suit the acetate rayon. Indigoid vat dyes are used in preference to the more complex anthraquinone vat dyes, though a few of the latter, especially Caledon Jade Green XS (ICI), are very useful. The fabric is usually dyed in the standard lingerie shades with dischargeable disperse dyes, which in these depths are readily destroyed by the Formosul used for fixation of the vat dyes.

But when the depth of ground shade is increased difficulties arise, due not to any intrinsic chemical resistance of the dischargeable dyes used, but to the tendency for the normal Formosul–soda ash printing paste to spread by capillary action during the steaming operation, even in the presence of swelling agents. The difficulty can be overcome by using Formosul with barium thiocyanate as swelling agent, when good whites can be obtained on a full range of shades, including black. The illumination of such discharges is more difficult, and the affinity of the free leuco compounds of vat dyes for the fibre is relied on for adequate fixation. Though much work has been done, the style is still a technically hazardous venture. In this connection it is interesting to note that in 1941 British Celanese Ltd. obtained a patent[42] for the use of formamidinesulphinic acid (thiourea dioxide) as reducing agent in illuminated discharge prints of this nature.

The basic dyes, too, have their place in the application printing of acetate rayon, many of them appealing on account of their well known beauty and clarity of shade. In this connection the Astrazon (IG) dyes introduced just before the war are deserving of special mention.

Mention should also be made of the possibilities in printing of organic pigments fixed by means of resins of the urea–formaldehyde and melamine–formaldehyde types polymerised *in situ*. Employed with discretion they are undoubtedly useful, enabling, for example, utilisation of the outstanding beauty and fastness of the phthalocyanine pigments. The Aridye pigment colours may be given as examples of proprietary brands with which good work on acetate rayon has been carried out. Combined with other printing styles, they should add to the versatility of the printing of acetate rayon goods.

It will have been noticed, in the course of this paper, that the solvents and swelling agents used are in the main freely soluble in water. In our view this is is a most important feature, since easy and complete removal on washing is economically and physically desirable. In the swollen condition the fibre is naturally weak, and accordingly must be carefully handled, but swelling should be limited to a degree which enables the fibres to regain most of their original physical structure and tenacity on washing off and drying.

## CONCLUSION

The disperse dyes have been established for a quarter of a century as the "bread-and-butter" dyes of acetate rayon, but in spite of obvious weaknesses the introduction of improvements in both this and the duosol type appears to have lost much of its early impetus; indeed many of those now in daily use were among the first to be introduced. Limitations imposed by the fibre itself, which demands dyes of limited molecular dimensions and high activity, militate against solution of some of the outstanding problems, and one wonders whether the chemist can find other useful chromogens not already exploited. Perhaps the introduction of the newer synthetic fibres—nylon and Terylene among them—will supply the necessary new impetus to this search, and enable nylon thereby to repay, at least in part, the debt it undoubtedly owes to acetate rayon.

The possibilities of mass dyeing by incorporation of dye or pigment in the spinning solution have always attracted some attention, and coloured yarns of the highest fastness, meeting all requirements, are available. These mass-dyed yarns are of considerable value as speciality yarns, but difficulties inherent in supplying a wide range of shades in a wide range of yarn qualities prohibit their exploitation for normal requirements. This is but one aspect of the search for improved colorations to meet the widening demands for specialised fastness properties, including fastness to the various treatments to which yarns and fabrics are subjected during manufacture. The vat, acid, and mordant dyes may all be applied to the swollen fibre with this object in view, but with results not always reaching the expectations of the investigators. The fastness of those vat dyes which are so applied seldom reaches that achieved on cellulose fibres or of the same dyes incorporated as pigments in the spinning solution. The acid dyes, including the premetallised acid dyes, often have useful wet fastness properties and may be of interest on this account, but those which require special mordant treatments are of little interest. Both vat and acid dyes have been used to a small extent on an industrial scale.

An equally important aspect in dyeing is the modern desire for processes which speed up and cheapen production whilst maintaining reasonable and acceptable standards of fastness. Although it must be admitted that acetate rayon does not lend itself to rapid dyeing processes so readily as do the cellulose fibres, promising results have been obtained with solvent dyeing methods, which have achieved some measure of success in America. Disperse, duosol, and acid dyes have been used.

Progress in printing acetate rayon has been steady, assisted by elucidation of the structure of cellulose and its derivatives; acceptance of the limitations of acetate rayon has also been accompanied by a growing realisation of its potentialities. Those dyes which have natural affinity for the fibre are readily applied by printing methods. Selected vat dyes are also in regular use, and can be applied in full shades quite satisfactorily when a swelling agent such as sodium thiocyanate is used as a constituent of the printing paste. They have also been used in lingerie prints for many years, but illuminated discharge printing on acetate fabrics in any but pale shades is still a difficult task.

It is in printing rather than in dyeing that advantage can be taken of controlled swelling of the fibre to achieve the desired results. This expedient is applicable to all styles, but becomes of greater interest for the duosol, or better still the acid, dyes, which should supersede the disperse dyes on both manipulative and fastness grounds as their possibilities become better known. In printing, as in dyeing, the possibility of effecting economies by speeding up production is always

attractive. Such a step as dispensing with the steaming operation has been recognised as a possibility and has been utilised, the small additional cost of ingredients being balanced against labour and other costs.

We are confident that the outstanding problems in the coloration of acetate rayon, though formidable, will eventually yield to the many workers in this field, and we take this opportunity of acknowledging our indebtedness to that large army of investigators who, contributing their quota to the sum of human knowledge, must for various reasons remain anonymous.

* * *

Our thanks are due to the Directors of British Celanese Ltd. for permission to publish this paper.

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## Discussion

Mr. W. CLARKE: Reference is made to the use of aqueous methylated spirits in oxidation blacks which contain a mixture of aniline and *p*-aminodiphenylamine. What are the reasons for the use of the mixture, in view of the fact that the rate at which the two amines oxidise in the presence of acid varies considerably? A printing paste of the above type would not be expected to be very stable. How would a black produced by using one of the recently described sulphamic acid derivatives of *p*-aminodiphenylamine compare with the former mixture? These sulphamic acid derivatives appear to be printed from a paste containing up to 10% thiodiglycol, which should have a similar fibre-swelling action to the aqueous methylated spirits.

Mr. MELLOR: Mixtures of *p*-aminodiphenylamine and aniline have long been used for printing oxidation blacks in the calico printing industry, where suitable mixtures are marketed under such names as Diphenyl Black Oil DO. *p*-Aminodiphenylamine alone will give excellent blacks, but aniline alone is relatively difficult to oxidise on acetate rayon. A mixture of the two bases is satisfactory, and is cheaper; and, of course, oxidation blacks of this nature are ungreenable.

The recently marketed sulphamic acid derivatives of the aminodiphenylamines can be oxidised on acetate rayon, but our experience of them is as yet very limited.

Mr. C. P. ATKINSON: Could the molten metal process be used for the rapid dyeing of acetate rayon fabrics?

Mr. G. L. BOARDMAN: Our main business at Standfast is the dyeing of high-class furnishing fabrics with vat dyes. Consequently we have concentrated on developing a process suitable for this class of work. Having established such a process, we are naturally interested in applying the molten metal technique to other classes of dyes and fibres, including cellulose acetate. Preliminary work in the laboratory has shown considerable promise. Satisfactory results have been obtained with acetate rayon dyes; also vat dyes have been applied without the use of swelling agents, and with practically no saponification of the acetate. Our present bulk machines were designed for processing cotton materials, and the ancillary equipment is not tensionless. This, therefore, makes the range in its present form unsuitable for processing light acetate fabrics. It is wrong,

however, to assume that a fabric passing through molten metal must necessarily be subjected to undue tension; this is not so. We feel that suitable modification of the existing technique would overcome this problem, and would enable materials of this type to be handled satisfactorily. Until we have had an opportunity of doing considerably more bulk experimental work we prefer not to express a firm opinion to the trade.

Mr. F. SMITH: Sonic waves cause rapid exhaustion and good penetration of Celliton Fast dyes. Would their application be of use in the continuous dyeing of acetate rayon yarn or fabric?

Mr. MELLOR: It appears that ultrasonic vibrations can be used not only in scouring [43] and dyeing [44] textile materials, but also in such operations as disintegrating textile fibres [45] and effecting greater orientation of the micelles in the spinning operation [46]. They have been claimed to speed up any textile operation taking place in a liquid medium. The available equipment imposes very severe limitations on their use.

Mr. C. L. BIRD: Is the principle involved in the solvent swelling process for dyeing acetate rayon with acid dyes as follows? The rayon is first swollen sufficiently to admit relatively large dye molecules, the exit of which is then prevented by rapid removal of the swelling agent. In this way a water-soluble dye is held mechanically within a fibre for which it has little or no affinity.

Mr. MELLOR: The mechanism suggested goes a long way towards explaining the essential phenomena of solvent dyeing and printing. We would suggest, however, that the composition of the imbibed liquid, and the fact that it is imbibed, are as important as opening up the fibre structure. Many acid dyes having little or no substantivity from aqueous dyebaths but applicable by solvent dyeing methods are substantially of the same molecular sizes as the duosol dyes.

Mr. R. THORNTON: The need for considerably higher wet fastness properties for ladies' underwear has long been recognised, and adequately met by normal vat printing methods as the designs are small, but the recent pronounced demand for two-way stretch acetate–Lastex yarn bathing wear has presented printers with a difficult problem to solve, the more so as the patterns are bold multicolours with a high percentage cover of vivid head colours and dark blotches. What are the best methods of meeting such a demand?

Mr. MELLOR: For two-way stretch acetate–Lastex yarn bathing wear, dyeing with direct disperse-type dyes is unsuitable, because in general they are not fast to the chlorinated water used in swimming pools. For such bathing wear which has to be printed with bold, full shades, we would recommend the use of selected vat dyes, e.g.—

Durindone Blue 4BCS (ICI)
Caledon Yellow GKP (ICI)
Paradone Jade Green XS (LBH)
Ciba Red 2B (Ciba)

applied with the addition of up to 15 parts of sodium thiocyanate per 100 in the print paste, followed by steaming for 30 min. at 220°F. Oxidation with 1 g. sodium percarbonate per litre at 60°C., acidified with acetic acid to pH 6, for 10 min. is followed by a rinse with cold water, then a soap at 60°C. in 0·5–1·0 g. soap per litre.

Mr. C. W. SEELEY: In the application of solvent dyeing methods to printing, is it not probable that the fibre will become plasticised, causing adhesion of the threads of the weave and rendering the fabric stiff and brittle where the colour is applied? Could the authors recommend a suitable solvent for acid dyes which will act as a swelling agent for the acetate rayon without causing it to become adhesive during steaming?

Mr. MELLOR: Plasticising of the fabric to the extent that adhesion of the individual fils and threads takes place must be avoided at all costs. We have attempted in our paper to indicate some suitable solvents and solvent mixtures which give the requisite amount of swelling whilst avoiding this pitfall. For fabric printing using aqueous printing pastes from which the water can be evaporated by drying, it is preferable to use water-soluble swelling agents, and to apply them in safe proportions only. They vary widely in properties, both when used alone and when used in admixture, and many do not give a sufficient margin of tolerance to be used safely.

Some mixtures of methylated spirits, water, and ammonium thiocyanate are imbibed immediately by the fibre, giving a good surface print but little penetration; whereas a mixture of equal parts of diethyl tartrate, urea, and ammonium thiocyanate gives adequate penetration together with good colour yield.

Mr. R. K. FOURNESS: Several disperse-type dyes, e.g. Duranol Blue 2G, have very desirable fastness properties but are only used on a limited scale because of their poor affinity and bad temperature range properties. Are their weaknesses overcome by applying these dyes by a solvent swelling technique? If so, would the authors consider it worthwhile, for the sake of the extra fastness to light, gas fumes, etc. thus obtainable, to apply them in this way; or, once having decided to use solvent swelling, would they select dyes from other classes altogether?

Mr. MELLOR: The superior fastness properties of disperse dyes of the Duranol Blue 2G type, particularly to gas fumes fading, is well known, and should be exploited wherever possible. In our Spondon dyehouses we accept its dyeing deficiencies in the interests of fastness, and it has long been our standard blue for underwear shades. The value of a dye for solvent dyeing and printing is governed by its solubility in the solvent mixture. Many of the disperse dyes are not sufficiently soluble in the cold padding liquor for general use, and Duranol Blue 2G is unfortunately numbered among those having low solubility in many organic solvents. We have had little first-hand experience of solvent dyeing in bulk with either disperse or acid dyes, but in printing we are making real progress with the use of duosol and acid dyes in order to utilise their

superior fastness to washing, marking off, and bleeding.

Dr. W. SHAW: It is recognised that the quantity of printing paste per unit area of fabric applied in machine printing may vary considerably for a number of reasons. Has it been found possible, when printing acetate rayon with acid dyes in the presence of solvents or swelling agents for the fibre, to devise standard recipes such that these variations in the amount of reagent deposited on the fabric do not result in damage to it in some cases, or reduction in the amount of dye fixed in others?

Mr. MELLOR: The primary aim in the use of swelling agents is to increase the receptivity of the acetate rayon to an amount comparable with, for example, cellulose fibres. It is also essential for repeatability of results to aim at complete fixation of the dye. This maxim applies to solvent printing on acetate rayon as much as to the many printing styles on other fibres. In a printing paste containing both dye and swelling agent, therefore, the mechanical problems of levelness or "shading" are no more acute than in other application printing styles. It is, however, expedient to make adjustments to both solvent and dye contents of the printing paste according to the type of fabric and depth of engraving in roller printing. In a similar way, the increased amount of paste applied in screen printing will also demand adjustment of solvent content. Much depends on choice of solvent, suitable mixtures giving ample latitude for exploitation by both roller and screen printing.

Mr. E. E. BOWKER*: In the dyeing and printing of cellulose acetate rayon, what are the relative merits and efficiency of water-soluble swelling agents as compared with water-insoluble swelling agents?

Mr. OLPIN*: Swelling agents which are very soluble in or completely miscible with water are preferred, not only because they do not lead to complications in the preparation of the padding liquor or printing paste, but also because their rapid and complete removal is essential if the swollen fibres are to resume their original form and tenacity. Water-insoluble swelling agents would also be substantive to the fibre and, if any quantity is left in, must necessarily be detrimental to its physical properties.

* Communicated

# The Prospect Before Us*

J. G. Evans

Modern processes of continuous dyeing are reviewed, and an estimate is made of future trends in the dyeing industry.

In this Festival Year it is the custom at most scientific gatherings of this nature to review the appropriate events of the last century. That, indeed, would have been a more palatable task than to peer into an uncertain future. When, however, I contrast my position with that of a chemist in the year 1851 and consider what he might have said of the prospect before him, I am heartened and emboldened by the general richness of our scientific experience. He, indeed, was faced with an unremitting vista of natural and inorganic colouring matters, and he would have been a remarkable prophet had he foreseen the discovery of the synthetic dyes and the growth of a great dye industry.

Were our early chemist to leap forward another fifty years and stand at the threshold of this century, he would have behind him the discovery of the direct and developed dyes, the sulphur dyes, and the acid and mordant dyes, yet it would have been beyond him to predict the vat dyes, and azoic dyes and their various forms, still less the disperse anthraquinone types.

Idle browsing in the 1900 issues of our *Journal* is salutary. I find no bold prophets scrutinising distant horizons.

It is true that a certain Dr. Brunck of B.A.S.F. suggests that Hindus might be better off growing food on land then devoted to producing natural indigo, but no less an authority than Ivan Levinstein states that there are two sides to this question and that to follow Dr. Brunck's advice may be suicidal folly. Worse still, in a later issue in rebuttal of the suggestion that synthetic indigo might replace the natural product, the *Journal* states: "That is not the opinion of the very ablest experts in Yorkshire". I pass on to you without comment that the same article states that "synthetic indigo is making more headway in Lancashire than in Yorkshire".

I make one more quotation from the 1900 *Journal*. Khaki had just been introduced to the army. The *Journal* quotes—

> "Whether khaki proves a possible uniform material remains to be seen. A high military authority has expressed the opinion that the material could never be used in home service. 'It soils so easily', he said, 'that you will never get a soldier to be content with it'".

All of which goes to show that the way of a prophet, like that of a transgressor, lies hard. I am all too conscious, therefore, that in surveying what lies before us I may well err in a prediction or invite criticism. So be it.

There will be general agreement that the last fifty years have been a period of high organic endeavour in our field. Research in synthetic dyes has been intensive and successful, but it has been by no means paralleled by a corresponding effort in the field of application. The turning point has, however, been reached. Research into dyeing methods is increasing, and the next half-century will see more major strides in application than in the production of new dye ranges, although improvements in application will achieve maximum success only if they are accompanied by appropriate dye studies.

The main immediate trend of dyeing research is abundantly clear. For so long dyeing has been in most cases of a batchwise character that the desire to process continuously is inevitable, for mass production methods are part of the pattern of modern industry. The march of external events is, however, by no means the important urge to continuity of production. It is believed that it will lead to—

1. Technical improvement, e.g. greater uniformity of shade over the complete dyeing lengths as well as greater levelness across the piece.
2. The elimination of shade variations from standard arising in different batches.
3. Higher rates of production.
4. A decreased man-hour consumption per unit length of fabric.
5. A reduction in D. and K.

These are cogent reasons at any time for new methods, but in a world of high and increasing materials cost and diminishing working hours, they become much more pressing.

In considering continuous methods it is clear that kinetics plays a major part. We must either apply the available dyes under conditions which favour much more rapid dyeing than normal or seek new dyes which have very high dyeing rates. The most potent factor controlling speed of dyeing with available dyes is temperature, and the most successful and promising continuous methods we have before us utilise the principle of control by temperature. Thus we have the pad–steam process, the Standfast molten metal process, the hot oil process, and the Uxbridge high-pressure process as wet methods, and the Thermosol process as a dry method. All other factors involved in these methods are subsidiary to the temperature effect and are mainly mechanical, designed to secure the level application and thorough penetration of the dye before the high dyeing speed fixes the dye *in situ*. All concepts of levelling by dyeing vanish. There is no room for levelling by transfer in a continuous process.

It is natural, too, that vat dyes, being the most rapid dyeing on cellulose as a class and highly

* This paper was not included in the preprints circulated before the Conference.

individualistic in character, should be exploited chiefly, thereby turning a disadvantage by long bath methods into an asset and carrying out dyeing so quickly that individualism has no time to assert itself. This also clearly widens the scope of shading components from dyes which could not be mixed in long dyeing processes, as, for example, so called "cold-" and "hot-dyeing" dyes.

This topsyturvydom in our approach to modern dyeing is of considerable importance and not least to those whose duty it is to provide us with dyes. The classical method of selecting candidates based on genteel dyeing behaviour from a long bath goes overboard in favour of the dye which exhibits bull-at-a-gate tactics. This behaviour is frequently associated with the technique in which the dye is first presented to the fibre in a condition wherein no affinity factors operate, as in pigment padding followed by rapid dyeing *in situ*. It is, however, by no means confined to this method, and now operates where the first and only contact of the cloth with the dye is with the leuco form. Since only some 1·5% of the speculative new vat dyes made find their way to the market, one wonders how many of the 98·5% consigned to the scrap heap, and of the accumulation of fifty years of vat dye research, would fit in more readily with present ideas on application.

It is pertinent to review these continuous methods in practice and under development and to discuss their possible future.

### PAD–STEAM PROCESS

In its usual form this involves padding cotton or viscose rayon fabric through a suspension of a vat pigment, drying (this stage is optional), impregnating with an alkaline reduction bath, and steaming, followed by the usual developing and clearing treatments. Variations include alkaline leuco padding and steam fixing, and acid leuco padding, followed by alkaline impregnation and steaming. It is applicable both to vat dyes and to sulphur dyes. It is relatively widely used in the U.S.A., but appears to have found little favour here, and although a similar process has been developed in Germany, it appears not to have found wide adoption yet in Europe generally.

There is an impression that the pad–steam process is confined to pale to medium shades. This is incorrect, since very full shades can also be dyed. The necessity for runs of the order of 3000–5000 yd. to a shade and the general economics of the process retard its development here. The method might become more popular if an efficient steamer were available at moderate cost.

### STANDFAST MOLTEN METAL PROCESS

There is no need for a detailed description of this process, especially as there is a special paper on it at the Conference. Here, again, vat dyes are applied at temperatures in excess of normal, and consequently at such a rate that dyeing is completed in a matter of seconds. Ingenious advantage is taken also of the molten metal to act as a fluid mangle to express liquor out of the cloth and as a means of excluding air during dyeing. The performance of the machine is most impressive, as regards both output and quality. The ability to dye single pieces makes it outstanding in continuous production methods, and the extraordinary rapidity of switching over from one shade run to another is an achievement of no small technical merit.

Although there are limitations on the exclusive use of the machine for applying leuco vat dyes to compact fabrics, such as gaberdines and poplins, which necessitate the use of prepadding in the vat pigment, this development has a bright future which will not be limited to its present use, and as a British contribution to the tinctorial art it is most timely.

### WILLIAMS HOT OIL PROCESS

The dyer may well be repelled at the thought of the deliberate application of his natural enemy, mineral oil, to fabric, but it is being exploited as a heating medium for the speedy dyeing of vat dyes and sulphur dyes.

Vat dyes are either pigment-padded, dried, passed through a caustic–hydrosulphite bath, and fixed in the hot oil, or drying after pigmenting is omitted, or simple padding in the reduced vat is followed by the oil bath. Sulphur dyes are padded in the reduced state, being fixed by running through the hot oil bath. The function of the oil is purely one of rapidly heating the textile, and in the latest machine the oil is heated by steam at 50 lb./sq. in. to give oil temperatures substantially in excess of 100°C. The fact that the cloth is wet prevents deep-seated penetration of the oil, and subsequent scouring is claimed to remove it. No samples I have examined have contained less than 0·4% ether-extractable matter or more than 4%, a range which would not be very acceptable to British commission dyers' concepts of finished fabric specification. Improved technique will no doubt bring the figure down. The loss of oil per 100 lb. of cloth is, by American standards, negligible, viz. 1 gallon, say ¼c. per yard of 4-oz. fabric, but the price of mineral oil here, as well as the difficulties of effluent disposal, may adversely affect the economic picture. However, this is a process which in its infancy is operating on a substantial scale in U.S.A. and cannot lightly be dismissed from future exploitation here.

### UXBRIDGE HIGH-TEMPERATURE MACHINE

This machine has been designed by the Backmann Uxbridge Worsted Corpn. primarily for dyeing wool continuously. The acid dye is padded on to the wool, which is passed rapidly through a pressure chamber at 15–20 lb./sq. in. and approx. 275°F. Dyeing is stated to be complete in about one minute, and it is claimed that the dyed fabrics have fastness, tensile strength, and other physical characteristics equal or superior to dyeings obtained by normal methods.

Clearly, this principle is of some general importance. The ability to treat under slight pressure could be advantageous in many dyeing operations on a variety of fibres, old and new. Capital cost of such a plant may, indeed, be high, and some bold decisions will be called for before plant of this nature is adopted.

THERMOSOL PROCESS

This process has been called forth because of the difficulties associated with the dyeing of the hydrophobic fibres, notably Orlon and to a less extent Terylene. The process consists in applying a dye solution or suspension to the fabric by padding or printing, drying, and heating for 5–60 sec. at 360–480°F. Under these conditions suitable dyes dissolve in the fibre.

Thus acetate rayon dyes and vat dyes as pigments may be applied to Terylene to give a depth and fastness unobtainable by normal dyeing methods. Indeed, vat dyes are normally inapplicable to Terylene.

Orlon can be coloured by acetate dyes and esters of leuco vat dyes, and nylon by acetate, direct, and acid dyes.

The process is clearly one involving some difficulty of control, but it must be regarded as a potential practical process, especially on fibres which have to undergo high-temperature setting, since it may be possible to combine setting and colouring in one operation.

It is clear that all the methods described so far use the same principle of quick heat transfer to secure rapidity of dyeing or coloration.

This basic idea will be employed for some time on continuous methods. It will be noted, however, that the success of the methods as regards levelness and penetration invariably depends on a standard mechanical padding operation of the dye in a form which lacks affinity for the fibre. There is still considerable scope here for improvement in the mechanics of the operation, and in the provision of dyes in a suitable form and especially for the elimination of migration during drying. Indeed, may it not be also that there are dyes still unexploited which are far more suitable for these high-temperature methods than existing dyes? The ideal is a dye of high solubility, of no affinity as applied, non-migratory if intermediate drying be necessary, and of ultra-rapid fixation subsequently.

The methods I have mentioned are on our doorstep. With the single exception of the molten metal process they owe their origin to foreign inspiration. That is indeed a reflection upon both our inventive capacity and our boldness of action in development. Tinctorial chemistry seems to have fallen into desuetude. There is but one chair of Colour Chemistry in the whole country. Technological research at the highest educational level is needed on a first-class scale to provide inspired entrants into our industry: Engineering research into the problems of the finishing industry is correspondingly weak. We need to initiate it forcefully at our universities and at our national research associations. The Society may well make a vital contribution to our future by inquiring into ways and means by which appropriate stimuli may be applied.

If speed be the essence of continuity, then colouring by chemical reaction *in situ* must obviously be considered. Indeed, some of the oldest methods of continuous practice, such as mineral khaki dyeing or aniline black formation, are examples of this. So, too, can be the more modern use of esters of leuco vat dyes and azoic couplings by padding methods. It is unlikely that these are the last examples of colour-producing reactions, and it is clear that there is considerable scope for new methods of colouring depending upon reaction *in situ*. Such reactions may be energy-activated by heat, light, or an atomic source. Indeed there have been abortive attempts to use light, but temporary failures with existing colouring matters need not deter the adventurous.

The reactions may be brought about, for example, by interaction between colourless bodies, the insolubilisation of dyes containing labile solubilising groups, or the use of ring-closing systems to provide fixation. There is ample scope, too, for improvement in what is known as dye fixatives, and it would be very advantageous to extend the metachrome principle to other soluble dyes by having a potential dye fixative not interacting with the dye initially and hence miscible with it but capable of later interaction—possibly under the influence of heat—so as to secure fixation.

Perhaps, however, the most profound single influence on the course of future dyeing will lie in the discovery of fibres from synthetic materials. The rayons have already stimulated a vast amount of work both on dyes and on methods of application, and what we have learned there has had its repercussions over the whole field of dyeing. It is certain that the newer fibres will demand an even greater effort. They cover a much wider range of chemical types, which call into play every feature of dye-fibre combination; their fine structure varies from the relatively easily penetrated elastic nylon to the highly organised compact structure of Terylene with its slow dye diffusion rate. That we shall have to deal with them in large quantities during the next half-century is unquestionable. In the short space of twenty years man increased the world production of rayon from 15,000 to 1,500,000 tons a year, and later ousted wool from its place as second only to cotton as an apparel fibre. By the end of 1952 America alone will be making fibres from synthetic sources to the extent of half its annual consumption of wool, to wit at a rate of 150,000 tons a year.

If rayon presented a challenge to the dyer, then many of the new fibres are a direct defiance of him. Indeed, it is quixotic—or perhaps it is not—that so many fibres of no little difficulty in dyeing behaviour are being produced by firms traditionally associated with dye manufacture.

These new fibres are a tremendous stimulus to dyeing research, and since so much is known of their structure their contribution to fundamental knowledge on dyeing will be immense. The problem of colouring them can be tackled in several different ways, thus—

1. Discovery of ways and means of applying existing dyes
2. Discovery of new dyes
3. Modification of structure to provide dyeing properties
4. Introduction of a dye acceptor, or mordant
5. Mass coloration.

There is no doubt that all these will be exploited and that individually or jointly they will solve the problems. Clearly Method 1 is the most readily available, and indeed some of the inspiration for high-temperature dyeing mentioned earlier arises from the response of some of the synthetic fibres to this method.

The use of swelling agents is another line of approach, but I do not see the widespread adoption of this method, partly because of the difficulties of handling swollen fibres, secondly because swelling may disorganise the fibre structure, and thirdly because of possible difficulties in removal.

On the other hand, the carrier technique offers greater promise. There are certain substances, e.g. *p*-phenylphenol in the case of Terylene, which appear to have no swelling action on the fibre, but which convey or carry other substances into the fibre. The difficulty of clearing this type of body remains, but a carrier is much less troublesome than is a swelling agent when left in a fibre.

As for Method 2, there is an undoubted need for inspired colour chemistry to produce new dyes or substances capable of forming colours *in situ*. We desperately need a new Perkin to provide new chromogens and chromophores.

Some of the new fibres are exceptionally durable. They will long outlast the life of the colouring matters applied to them. Orlon, for example, is exceptionally resistant to weathering and destructive processes such as bacterial or mould attack, being far ahead of other fibres in these respects. Nylon is outstanding in its resistance to abrasion and general wear and tear. One can imagine nylon outer garments long outlasting their counterparts in other apparel fibres. Do not these attributes call for dyes of exceptional fastness, too? May it not be, therefore, that we shall require a very substantial increase in dyes of high light fastness in pale to medium shades, as well as a selection of dyes of the highest grade of fastness in full shades. They are notoriously absent from existing ranges. Thus, for example, in a pattern card exhibiting dyes for nylon there were one disperse dye out of 25, five acid dyes out of 35, seven chrome dyes out of 15, and two direct dyes out of 20 with a light fastness of 6 or higher in deep shades. The standard here was not *B.S.* 1006 but a comparable 8 scale. The dyes available in the above were for one reason or another not altogether suitable for many uses and of generally moderate fastness in pale to medium depths.

In another maker's range twenty acid dyes out of 140 reached 6 (*B.S.* 1006) in deep shades, but of these twenty, ten were blues. For many new fibres a light fastness standard of 6 in deep shades with a substantial drop in medium and pale shades is not good enough.

This is a state of affairs which current and future dye research is bound to remedy. Indeed, there are indications already of new dyes of good light fastness on such fibres becoming available, but if they are accompanied by some defect in another direction such as sensitivity to washing conditions their appeal is correspondingly limited.

Surely, too, the new fibres with their tremendous number of possible chemical variants offer the possibility of introducing molecular changes which themselves may form part of a potential colouring system. That is to say, groups which on appropriate reaction with applied "developers" will provide colour.

Alternatively, the introduction of a dye acceptor or mordant during manufacture offers another way of colouring.

It may well be, however, that mass coloration will provide the answer to many problems and especially that of fastness. By this I mean the introduction of pigments or colouring matters into the substance from which the fibre is extruded, as, for example, the introduction of carbon black into viscose dope to produce a mis-called mass-"dyed" black. The introduction of mass-coloured rayon has been successful in many fields and, although small compared with the total volume of rayon production, is as a unit manufacture formidable enough and expanding. In the case of some of the synthetic fibres soluble colouring matters give shades of a clarity, depth, and fastness unobtainable by any other method. The commercial and technical limitations of this method of coloration are so well known that they need no elaboration, but under some favourable circumstances the method could be used on a very extensive scale.

If we succeed in many of these attempts, the repercussions on the whole of our technology will be fundamental. In the field of colour application itself new methods of recipe control of an automatic character may well be demanded with appropriate mechanical, optical, electronic, or other energy-activated devices with the maximum eradication of human judgment.

Instruments are available now for the measurement and control of temperature, pH, dyebath volume, and rate of addition of dye; the latest is a redox control system, which will inevitably be linked with a relay mechanism, which will add alkali or hydrosulphite to a dyebath according to requirements. Indeed, instrumentation has reached such a peak that it is no idle dream that, long before the end of this century, a standard dyeing may be placed before an optical scanning apparatus which will set in motion the whole operation of dyeing and its control.

On either side of the dyeing process there will have to be corresponding improvements in processing technique to provide a balanced output. Thus a dyeing operation which is over in a matter of seconds needs a preparing department to feed fabric to the dyehouse at an appropriate rate and a finishing shop to absorb its output at a corresponding rate. Nothing is more wasteful of capital expended on buildings than large areas devoted to cloth standing between operations, apart from other notable disadvantages.

In a properly balanced production there is a smooth and continuous flow of cloth throughout all departments. Events are to some extent foreshadowed in the most modern American dyehouses, where cloth leaves the loom to be continuously processed until it is made up and

parcelled some 48 hr. later. Long runs there may be and finishing demands may be modest, but as an ideal it is worthy of attainment.

In all this we need a new chemical, a new physical, and a new mechanical approach to our problems to provide the simplicity of push-button control, and particularly a new skill in management. Under such a system the dangers of overproduction are manifest, and the ever present problem of redundancy may well become acute.

I have, I admit, taken a mundane outlook on events, and have tended to look at what may happen immediately rather than survey the remoter scenes. If I let my fancy run free for a moment, I must begin by admitting that we live in a world in which the amount of free-will choice is steadily diminishing. There are large areas of the world with vast populations whose life and choice of action are regimented in no uncertain manner. Even in this country the loss of independent individual action as between now and twenty years ago is by no means unimportant. As life becomes more ordered and control more authoritative, government may pass to those who demand the highest efficiency. In a system of ruthless efficiency there is no room for the dyer or, indeed, for the spinner or weaver. Mass-coloured synthetic materials may well be extruded in such a manner as to eliminate both cloth manufacture and finishing. The world will be the poorer. Our contribution to the future in those circumstances may well be to provide the historian of 2051 with a record of the lost art of dyeing in 1951.

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In closing the Conference, Mr. F. Scholefield (*President of the Society*) expressed the Society's thanks to all those responsible for what was generally agreed to be one of the most successful among the Society's symposia and conferences.

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## ERRATUM

**Rayon Staple—A Dyeing Miscellany.** J. Boulton (J.S.D.C., **67**, 411 (Nov. 1951))—At the end of the first paragraph, the concentration of sodium hypochlorite (15% available chlorine) should be 0·66 c.c. per 100 c.c. liquor.

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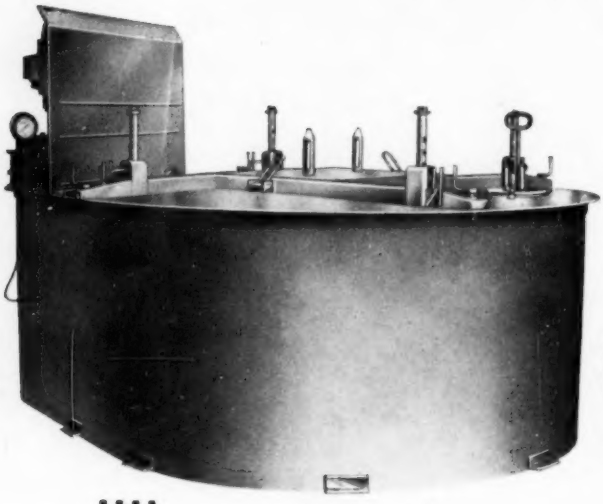

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## FORTHCOMING MEETINGS OF THE SOCIETY—*continued*

### Scottish Section—*continued*

1952

Tuesday 19th Feb. — R. A. Peel, Esq. *Turkey Red Dyeing in Scotland— Its Heyday and Decline*

Tuesday 18th March — ANNUAL GENERAL MEETING 7 p.m. LECTURE 7.30 p.m. J. Zonnenberg, Esq. *Recent Developments in Starch Products and their application to Sizing, Finishing and Printing*

### BRADFORD JUNIOR BRANCH

*All meetings held in the Bradford Technical College at 7.15 p.m.*

1952

Tuesday 22nd Jan. — STUDENTS' ANNUAL COMPETITION EVENING

Monday 18th Feb. — Dr. C. S. Whewell (Leeds University) *The Wet Finishing of Wool Textiles*

Thursday 28th Feb. — THE JUNIOR BRANCH DANCE at the Queen's Hall

Wednesday 5th March — J. A. Hepworth, Esq., B.Sc., A.T.I. (Shell Chemicals Ltd.) *Petroleum Derived Chemicals in the Textile Industry*

Saturday 8th March — Visit to Wool Industries Research Association, Torridon

Tuesday 25th March — E. E. Tallis, Esq., B.Sc., A.R.I.C. (Courtaulds Ltd.) *Recent Developments in Viscose Rayon and Staple Manufacture*

There will be a visit to Salts (Saltaire) Ltd., the date of which has not yet been fixed.

### LEEDS JUNIOR BRANCH

*All meetings to be held in the Colour Chemistry Lecture Theatre, Leeds University, at 4 p.m.*

1952

Tuesday 22nd Jan. — E. Stead, Esq., B.Sc. and A. Murray, Esq., B.Sc. (Yorkshire Dyeware & Chemical Co. Ltd.) *Some developments in Dispersed Azo Dyes for Acetate Rayon and Nylon*

### Leeds Junior Branch—*continued*

Tuesday 5th Feb. — B. Kramrish, Esq., or J. A. Potter, Esq. (The Clayton Aniline Co. Ltd.) *The Dyeing of Vinyl Polymers*

Tuesday 26th Feb. — Dr. F. L. Warburton (Wool Industries Research Association) *Colour Vision*

### MANCHESTER JUNIOR BRANCH

*All meetings commence at 6.30 p.m.*

1952

Friday 11th Jan. — S. Burgess, Esq., H. Hampson, Esq., and E. R. Lambie, Esq., *The Application of Vat Dyestuffs to Viscose Rayon Packages.* Reynold's Hall, College of Technology, Manchester

Friday 14th Mar. — Lecturer from the Bleachers' Association Ltd. Name later. *Progress in Textile Bleaching.* Reynold's Hall, College of Technology, Manchester

### WEST RIDING SECTION

*All meetings held at the Great Northern Victoria Hotel, Bradford, at 7.15 p.m. unless otherwise stated*

1952

Friday 18th Jan. — LADIES' EVENING

Thursday 31st Jan. — Dr. G. H. Lister (Sandoz Products Ltd.) Title later

Thursday 14th Feb. — G. G. Taylor, Esq., B.Sc., A.Inst.P. (Clayton Aniline Co. Ltd.) *Uses of Microscopy in Textile Dyeing and Finishing*

Thursday 28th Feb. — Dr. A. S. C. Lawrence (Dept. of Chemistry The University, Sheffield) *Detergents* (exact title later)

Tuesday 4th March — T. Thorne Baker, Esq. (Director of Research, Dane & Co. Ltd.) *Fluorescent Dyestuffs and the Application of Fluorescent Textiles.* Metropole Hotel, Leeds

Thursday 13th March — Details later

Thursday 27th March — ANNUAL GENERAL MEETING

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Inman, E., 30 Carlinghow Lane, Batley, Yorkshire
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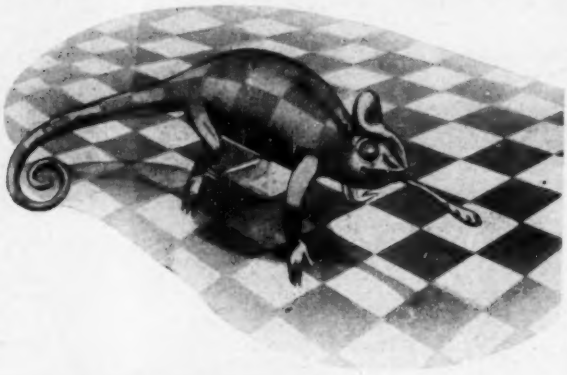

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The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion in this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

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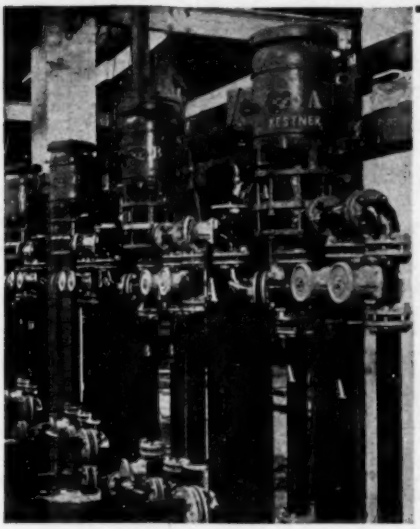

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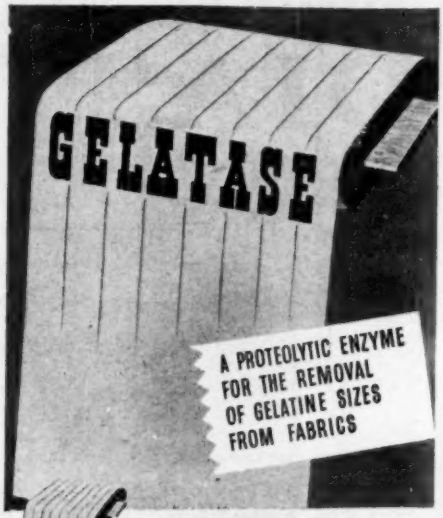


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# Review of Textile Progress
## Volume 1

Compiled and published jointly by the Textile Institute
and the Society of Dyers and Colourists

*Editors*

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*The Textile Institute and the Society of Dyers and Colourists have jointly published a Review of Textile Progress, Volume 1 relating particularly to the year 1949. There are 24 contributors in the Review and the authors are experts in the various sections for which they are responsible*

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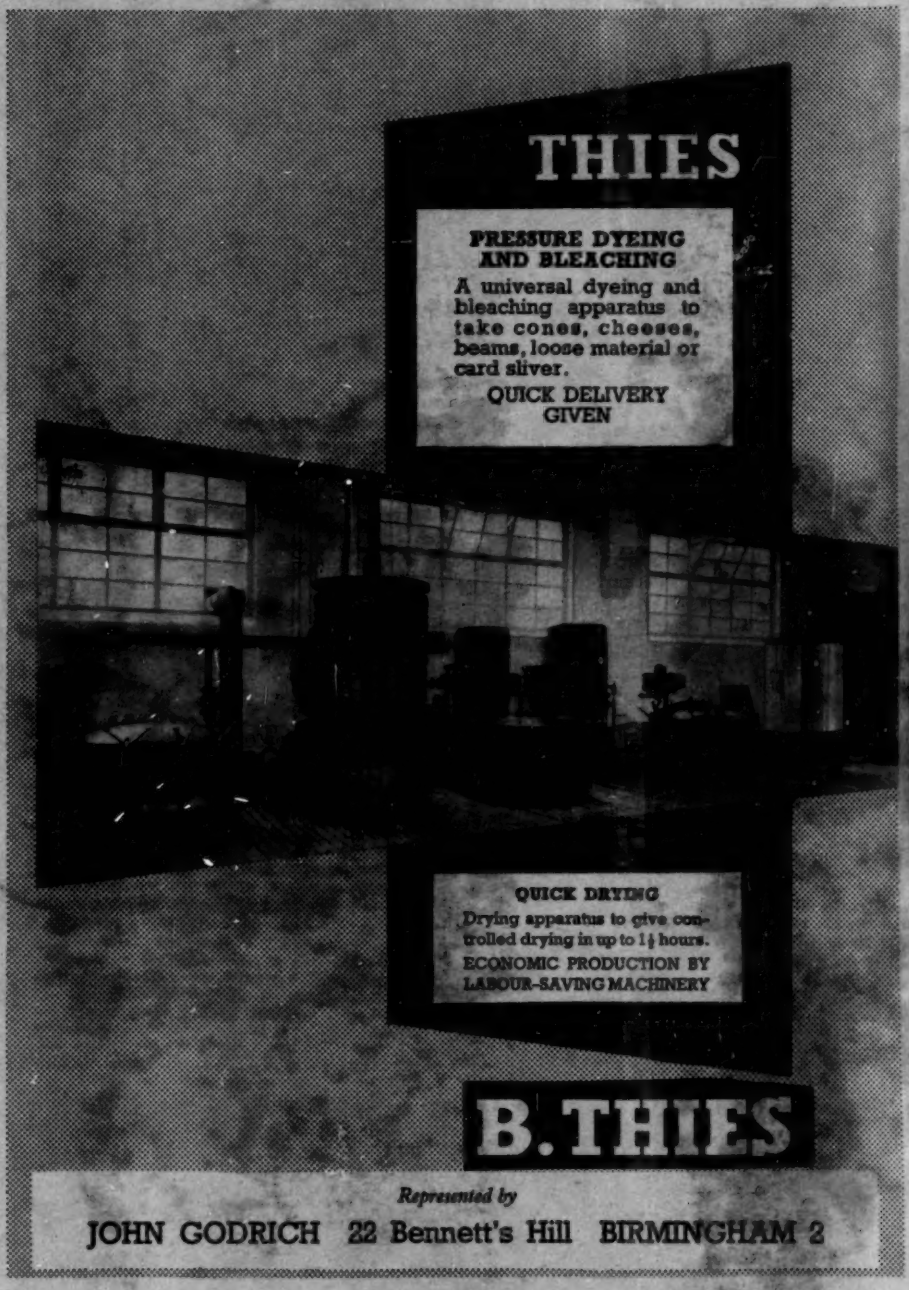
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